Poisonings due to consumption of honeys containing plant toxins have been reported worldwide. One cause in New Zealand is the neurotoxin tutin, an oxygenated sesquiterpene picrotoxane, traced back to honey bees (Apis mellifera) collecting honeydew produced by passionvine hoppers (Scolypopa australis) feeding on sap of the poisonous shrub tutu (Coriaria spp.). A recent pharmacokinetic study suggested that unidentified conjugates of tutin were also present in NZ toxic honeys.

We have discovered two tutin glycosides in NZ toxic honeys using ion trap LC-MS. These were purified and their structures determined as 2-(β-D-glucopyranosyl)-tutin (1, see above) and 2-[6′-(α-D-glucopyranosyl)-β-D-glucopyranosyl]-tutin (2). This discovery led to the lowering of the maximum permitted concentration of tutin in honeys from 2 mg/kg to 0.7 mg/kg.

We had thought that the glycosidation of tutin might represent detoxification of the plant toxin by one or both of the insects involved in the food chain from plant to honey. However, a quantitative LC-MS study showed that tutin, hyenanchin and both tutin glycosides 1 and 2 were present in tutu phloem sap at similar concentrations and ratios to those found in honeydew and honey. Therefore the tutin glycosides were of plant not insect origin, and diglycoside 2 could be a transportable tutin form between source and sink plant tissues in tutu.

Good quantities of glycosides 1 and 2 were needed as reference standards for food safety analyses. We attempted to synthesise glycoside 1 from tutin, available reasonably readily from tutu leaf. We were only able to obtain α-glucoside derivatives, and rearrangements of the tutin core complicated the chemistry.

References
(1) Goodwin, M. A New Zealand history of toxic honey; Lightning Source UK Ltd.: Milton Keynes, UK, 2013.