

## Novel Cleavage of the Glycosidic Bond of Saponins in Alcoholic Alkali Metal Solution containing a Trace of Water

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Treatment of saikosaponin c (**8**) with alcoholic alkali metal solution containing a trace of water afforded the sapogenin saikogenin E and three new partially hydrolysed prosapogenins in satisfactory yield.

When saikosaponin d (**1**),<sup>1,2</sup> was acetylated with acetic anhydride-pyridine the hepta-acetate (free 16 $\alpha$ -OH) was obtained, which was oxidized with chromic anhydride in pyridine; deacetylation with 2% NaOH in methanol under reflux for 1 h gave the new compound (**2**), m.p. 240–243 °C,

$[\alpha]_D + 29.7^\circ$ , almost quantitatively. Compound (**2**) was reduced with sodium borohydride in methanol to give saikosaponin d (**1**) quantitatively, but reduction with sodium metal in absolute alcohol (MeOH, EtOH, or Bu<sup>n</sup>OH) gave saikosaponin a (**3**)<sup>1,2</sup> quantitatively. If the spectroscopic grade of the alcohols was employed as solvent in the latter reaction, five compounds were obtained in addition to starting material (**2**). Three were identified by comparison with authentic samples as saikosaponin a (**3**), prosaikogenin (**4**),<sup>3</sup> and saikogenin F (**5**),<sup>3</sup> and the structures of the remaining two new compounds were determined to be (**6**), m.p. 238–241 °C,  $[\alpha]_D + 41.4^\circ$ , and (**7**), m.p. 245–247 °C,  $[\alpha]_D + 26.0^\circ$ , mainly on the basis of <sup>13</sup>C n.m.r. data. This suggests that the glycosidic bonds were cleaved during the reduction with alkali metal (Na or K) in alcohols containing a small amount of water.

To investigate this reaction further sodium metal (1 g) was dissolved in absolute ethanol (10 ml) and absolute ethanol (10 ml) containing saikosaponin c (**8**) (100 mg) was added. The mixture was left overnight at room temperature and no reaction was observed. A drop of water (ca. 0.1 ml) was then added, and the mixture left for 36 h; t.l.c. of the mixture showed five spots. Water (100 ml) was added and the mixture was extracted with n-butanol (150 ml). The butanol layer was washed ( $\times 3$ ) with water and evaporated to dryness to leave a colourless solid, which was purified on silica gel with chloroform-methanol-water (65:35:10) to afford recovered saikosaponin c (**8**) (17.3%), saikogenin E (**12**) (23.4%), and three new prosapogenins E<sub>1</sub> (**9**) (8.4%), m.p. 221.0–222.5 °C,  $[\alpha]_D + 25.3^\circ$ , E<sub>2</sub> (**10**) (20.6%), m.p. 200.5–202.0 °C,  $[\alpha]_D + 24.7^\circ$ , and E<sub>3</sub> (**11**) (3.1%), m.p. 213.5–214.0 °C,  $[\alpha]_D + 42.6^\circ$ .

This reaction thus gives all possible partially hydrolysed prosapogenins and a sapogenin, which was very labile under acidic conditions, in reasonable yield.

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### References

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