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

Yukio Ogihara\* and Mitsuhiko Nose

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuhoku, Nagoya, Japan

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°, 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 BunOH) gave saikosaponin a  $(3)^{1,2}$  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°, and (7), m.p. 245–247 °C,  $[\alpha]_{D}$  +26.0°, 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 (×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°, E<sub>2</sub> (10) (20.6%), m.p. 200.5-202.0 °C,  $[\alpha]_D$  +24.7°, and E<sub>3</sub> (11) (3.1%), m.p. 213.5-214.0 °C,  $[\alpha]_D$  +42.6°.

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

Received, 12th May 1986; Com. 632

## References

- 1 T. Kubota, F. Tonami, and H. Hinoh, Tetrahedron, 1968, 24, 675.
- 2 T. Kubota, F. Tonami, and H. Hinoh, Tetrahedron Lett., 1968, 303.
- 3 K. Shimizu, S. Amagaya, and Y. Ogihara, *Chem. Pharm. Bull.*, 1985, **33**, 3349.