Studies on Orchidaceae Glycosides. 1. The Constitution and Relative Configuration of Dendrosteroside, a Steroid Glycoside from *Dendrobium ochreatum* Lindl.

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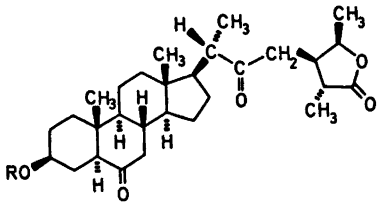
Three closely related crystalline glycosides have been isolated from *Dendrobium ochreatum* Lindl.[1] One of the glycosides ($C_{41}H_{64}O_{15}$), named dendrosteroside (I), crystallised from water as colourless needles, m.p. 239–245 °C (decomp.), $[\alpha]_{578}^{23}$ −32.5° (*c* 1.27, methanol). Sugar and methylation analysis [2] showed that the glycoside (I) contains a disaccharide moiety composed of two D-glucose residues, connected by a (1→6)-linkage. On enzymatic hydrolysis with emulsin, dendrosteroside (I) gave first a monoglycoside (II), m.p. 235–240 °C (decomp.), $[\alpha]_{578}^{23}$ −12.5° (*c* 1.39, methanol) and finally the aglycone III, named dendrosterone, m.p. 240–245 °C (decomp.), $[\alpha]_{578}^{23}$ +19.6° (*c* 0.74, methanol). This



I : R= ß-gentiobiosyl
II : R= ß-D-glucopyranosyl
III: R= H

evidence, together with the application of Hudson's rules of isorotation,[3] indicates that the sugar moiety in I is gentiobiose, β-linked to the aglycone (III).

The structure of dendrosterone (III) $C_{29}H_{44}O_5$, was determined by an X-ray direct phase determination procedure. The compound crystallises from methanol in the monoclinic space group $P2_1$ with $a = 17.551(2)$, $b = 7.280(1)$ and $c = 10.654(3)$ Å, $\beta = 104.64(1)°$, $Z = 2$. X-Ray intensity data were collected with the computer-controlled diffractometer Philips PW 1100. The phase determination was carried out by the direct phase method. A number of *E*-maps gave probable partial structures located in different parts of the unit cell. Phases calculated from one of these partial structures, the A, B and C ring-system, were used as a basic set for further phase determination. A new *E*-map was calculated which additionally displayed the five-membered ring and the lactone ring. The remainder of the structure was revealed by a combination of difference Fourier syntheses and least-squares refinements. The coordinates were refined to an *R* value of 0.058 with anisotropic thermal parameters assigned to all atoms other than hydrogen and fixed coordinates and isotropic thermal parameters assigned to the hydrogen atoms. Fig. 1 shows a perspective view of dendrosterone (III).

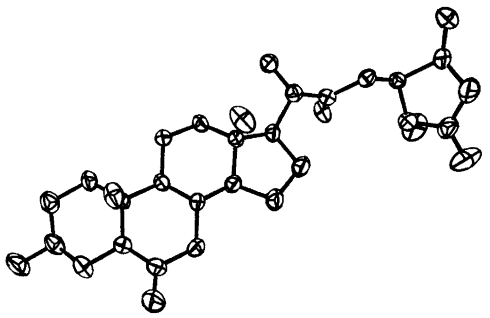


Fig. 1. A perspective view of dendrosterone (III).

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