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## CAMPESTERYL BEHENATE IN LIVERWORTS\*

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DURING our investigation of liverworts we isolated from *Calypogeia trichomanis* (L.) Corda an unknown compound of m.p.  $91^{\circ}-92^{\circ}$ .<sup>1</sup> We have now found the same product in *C. integristipula* Steph. and *C. muelleriana* (Schiffn.) K. Müll. and identified it as campesteryl behenate. Saponification of the ester yielded a neutral compound of m.p.  $156^{\circ}-157^{\circ}$ , identical with campesterol, and an acid of m.p.  $79^{\circ}-80^{\circ}$ , identical with docosanoic acid (= behenic acid). The occurrence of campesteryl behenate in these liverworts is of interest from a chemotaxonomical point of view, for so far this ester has only been found in *Calypogeia* species.

Calypogeia integristipula (250 g, collected in August 1973 in the Harz Mountains, Hohneklippen, 900 m a.s., DDR) was air dried, ground and extracted with Et<sub>2</sub>O. The extract was freed from Et<sub>2</sub>O and the residue chromatographed in C<sub>6</sub>H<sub>6</sub> on Al<sub>2</sub>O<sub>3</sub> (200 g, activity II, neutral). Elution with C<sub>6</sub>H<sub>6</sub> (11) and rechromatography in hexane on Al<sub>2</sub>O<sub>3</sub> yielded after crystallization from C<sub>6</sub>H<sub>6</sub> campesteryl behenate (2·0 g) in leaflets of m.p. 96°–98° and  $[\alpha]_{D}^{+}-14^{\circ}$  (c 1, CHCl<sub>3</sub>). C<sub>50</sub>H<sub>90</sub>O<sub>2</sub>. MS: 722 (M<sup>⊕</sup>), 382 [(M-C<sub>21</sub>H<sub>43</sub>CO<sub>2</sub>H)<sup>⊕</sup>] and 340 [(C<sub>22</sub>H<sub>44</sub>O<sub>2</sub>)<sup>⊕</sup>]. IR (in KBr): 724, 732, 775, 795, 810, 840, 855, 900, 930, 950, 966, 1005, 1020, 1030, 1062, 1090, 1112, 1135, 1172, 1184, 1204, 1218, 1238, 1250, 1270, 1282, 1300, 1330, 1380, 1418, 1468, 1724 (-CO–) and 2590 cm<sup>-1</sup>.

*Hydrolysis of campesteryl behenate.* Campesteryl behenate (0.5 g) in EtOH–C<sub>6</sub>H<sub>6</sub> mixture (40 ml, 1:1) was refluxed with KOH (2 g) for 3 hr and worked up in the usual manner. After chromatography on Al<sub>2</sub>O<sub>3</sub> and crystallization from CHCl<sub>3</sub>–MeOH the neutral part gave plates (0.2 g), m.p. 156°–157° and  $[\alpha]_{2}^{24}$ –38° (c 1, CHCl<sub>3</sub>), identical with campesterol. The acetate had m.p. 137°–139°. The acid fraction from the saponification gave plates of m.p. 79°–80° after crystallization from MeOH, identical with docosanoic acid. The methyl ester, CH<sub>3</sub>–(CH<sub>2</sub>)<sub>20</sub>–CO<sub>2</sub>CH<sub>3</sub>, had m.p. 53°–54°. MS: 353 [(M–H)<sup> $\Theta$ </sup>].

*Calypogeia muelleriana* was collected in August 1965 in the Ore Mountains, Pfahlbergmoor, 990 m a.s., DDR. Voucher specimens of all three liverworts are to be found in the herbarium of the author.

\* Part XVI in the series "Constituents of mosses and liverworts". For part XV see, HUNECK, S., SCHREIBER, K. and JÄNICKE, S. (1973) Phytochemistry 12, 2533.

<sup>1</sup> MEUCHE, D. and HUNECK, S. (1966) Chem. Ber. 99, 2669.