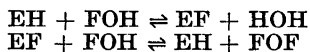


hydrolyzed with  $\beta$ -fructofuranosidase. Chromatography of the products of these reactions showed only a single fructose spot.

Fig. 2 shows a chromatogram of one of the substances (Fru-Fru<sub>1</sub>) before and after hydrolysis, together with sucrose, and 6- $\beta$ -fructofuranosylglucose and free fructose. No oligosaccharide formation was detectable when glucose was incubated with the enzyme preparation. The most reasonable mechanism of the reaction would seem to be:



Since fructose in glycosides always is present in the furanose form, and since we know that the  $\beta$ -fructofuranosidase transfers fructose to primary alcohol groups only, the two disaccharides probably are 6- $\beta$ -fructofuranosylfructose (levanbiose) and 1- $\beta$ -fructofuranosylfructose (inulobiose).

That fructose behaves as both donor and acceptor simultaneously supports the hypothesis of the existence of an intermediary enzyme-fructose complex, which, in turn, supports the hypothetical mechanism for sucrose hydrolysis mentioned above.

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## Synthesis of DL-Heptadecane-1,14-diol

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During studies on Compositeae ene-yne, Löfgren and Johansson<sup>1</sup> isolated the diacetate of oenanthotoxin, *trans*-heptadeca-2,8,10-triene-4,6-diyne-1,14-diol from *Centaurea montana* L. Oenanthotoxin had been previously found in *Oenanthe crocata* L. by Anet *et al.*<sup>2</sup> Complete hydrogenation of oenanthotoxin gives D-heptadecane-1,14-diol<sup>2</sup> and the enantiomer can be obtained from cicutoxin in the same way.<sup>2</sup> Although the racemate corresponding to oenanthotoxin has been synthesized by Bohlmann and Viehe,<sup>3</sup> no attempt has been made to synthesize the saturated diol in an unequivocal manner.

To synthesize DL-heptadecane-1,14-diol (I), the Grignard reagent of 11-bromo-1-undecene<sup>4</sup> (II) was reacted with oxirane to give 12-tridecene-1-ol (III), which was transformed to 13-bromo-1-tridecene (IV) by the action of phosphorus tribromide. Reaction of the Grignard reagent of IV with oxirane yielded 14-pentadecene-1-ol (V), which was oxidized to DL-pentadecane-1,2,15-triol (VI) by performic acid. Attempts to oxidize VI to tetradecanal-14-ol (VII) using periodate, periodic acid, or lead tetraacetate led to the formation of polymeric gums insoluble in most solvents except hot tetrahydrofuran (*cf.* Sisido *et al.*<sup>5</sup>). The method described by Raman<sup>6</sup> for cleavage of 1,2-glycols with "silver-iodide-dibenzoate" in benzene under anhydrous conditions, however, gave a satisfactory yield of VII. In air at room temperature, VII polymerizes rapidly, resulting in an increase of melting point and disappearance of the strong carbonyl band in the IR-spectrum. The hydroxyl group of VII was protected as a tetrahydropyranyl ether and the aldehyde group was allowed to react with propylmagnesium bromide; after hydrolysis DL-heptadecane-1,14-diol (I) was obtained. IR- and mass-spectra of I were identical with those of D-heptadecane-1,14-diol obtained by hydrogenation of oenanthotoxin,<sup>2</sup> kindly supplied by Dr. Lythgoe.

*Experimental.* Melting points are corrected. Boiling points are uncorrected. Argon was introduced during all distillations under diminished pressure. Infrared spectra were measured on an IR 8 Beckman spectrometer. Mass-spectra were recorded on an LKB 9000 mass-spectrometer, equipped for peak matching.

*12-Tridecene-1-ol (III).* The Grignard reagent of 140 g (0.600 mole) of 11-bromo-1-undecane (II) and 14.6 g (0.600 mole) magnesium was produced in tetrahydrofuran in the conventional way and cooled to 0°, then 28.6 g (0.650 mole) oxirane in tetrahydrofuran was added. During addition of the oxirane solution, the reflux condenser and the dropping funnel were cooled by solid CO<sub>2</sub>. After refluxing the mixture for 7 h and subsequent acid hydrolysis, III was extracted with benzene. After removal of the benzene, III was distilled; b.p. 102°–104°/0.1 mm Hg;  $n_D^{25}$  1.4532, (solidifying p. 8°–10°); yield 53.5 g (0.270 mole, 45 %). (Found: C 78.9; H 13.3. Calc for C<sub>13</sub>H<sub>26</sub>O: C 78.7; H 13.2).

*13-Bromo-1-tridecene (IV).* 12-Tridecene-1-ol (III) was reacted with phosphorus tribromide, as described by Diaper,<sup>4</sup> for the preparation of IV, yielding 43 % of 13-bromo-1-tridecene (IV), b.p. 100°–103°/0.2 mm Hg;  $n_D^{25}$  1.4684. (Found: C 59.5; H 9.65. Calc. for C<sub>13</sub>H<sub>25</sub>Br: C 59.5; H 9.65).

*14-Pentadecene-1-ol (V),* was prepared from IV in the same way as II was transformed to III, yield 49 %, b.p. 116°–120°/0.01 mm Hg;  $n_D^{25}$  1.4554 (supercooled); solidifying p. 25°–26°. (Found: C 79.3; H 13.4. Calc. for C<sub>15</sub>H<sub>30</sub>O: C 79.6; H 13.4).

*DL-Pentadecane-1,2,15-triol (VI).* 14-Pentadecene-1-ol (V) was oxidized with formic acid and hydrogen peroxide according to the method of Swern *et al.*<sup>5</sup> for oxidation of undecene-1-ol to undecane-1,2,11-triol, producing in 72 % yield pentadecane-1,2,15-triol (VI), which crystallized from ethyl acetate as colourless leaflets, m.p. 94°–96°. (Found: C 68.8; H 12.4. Calc. for C<sub>15</sub>H<sub>32</sub>O<sub>3</sub>: C 69.2; H 12.4).

*Tetradecanal-14-ol (VII).* Using conditions which excluded moisture, silver benzoate (12.2 g; 0.053 mole) and iodine (3.4 g; 0.12 mole) were stirred 1 h at 60° and, while hot, VI (6.9 g; 0.026 mole) was added. The mixture was refluxed 4 h, filtered and the benzene phase extracted with 10 % sodium hydrogen carbonate solution. After drying, benzene was

removed by freeze drying, leaving 4.1 g (0.018 mole; 66 %) VII as a white solid, m.p. 55°–56°. (Found: C 72.3; H 11.9. Calc. for C<sub>14</sub>H<sub>28</sub>O<sub>2</sub>: C 72.0; H 12.1). Spontaneous polymerization at room temperature raises the m.p. to 64°–65° in a month (*cf.* Hurd<sup>7</sup>).

*DL-Heptadecane-1,14-diol (I).* Tetradecanal-14-ol (VII) 4.1 g (0.018 mole) was transformed to the corresponding tetrahydropyranyl ether by conventional methods<sup>9</sup> in 63 % yield. Attempts to distil the tetrahydropyranyl ether resulted in extensive decomposition; consequently, the ether was treated directly with 0.012 mole propylmagnesium bromide. The reaction mixture was refluxed 6 h, hydrolyzed, and the resulting ethereal solution evaporated, leaving crude I as a white solid. Recrystallization four times from chloroform-light petroleum (1:7; v/v) gave 1.1 g I (0.0038 mole; 33 %), m.p. 61°–65° (recorded m.p. for the enantiomers 71°, and for a mixture of them 64°–65°). Pertinent mass spectra peaks: *m/e* 272 (M<sup>+</sup> small), 236.2504 (M–36), 229.2167 (M–43), 211.2062 (M–43–18), 193 (M–43–36) base peak. Calculated for: C<sub>17</sub>H<sub>32</sub> 236.25040, C<sub>14</sub>H<sub>26</sub>O<sub>2</sub> 229.21676, C<sub>17</sub>H<sub>27</sub>O 211.20619. (<sup>12</sup>C = 12.00000).

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