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Note

On the mechanism of the scission of the glycosidic linkage of methyl (methyl D-glucopyranosid)uronate induced by photolysis

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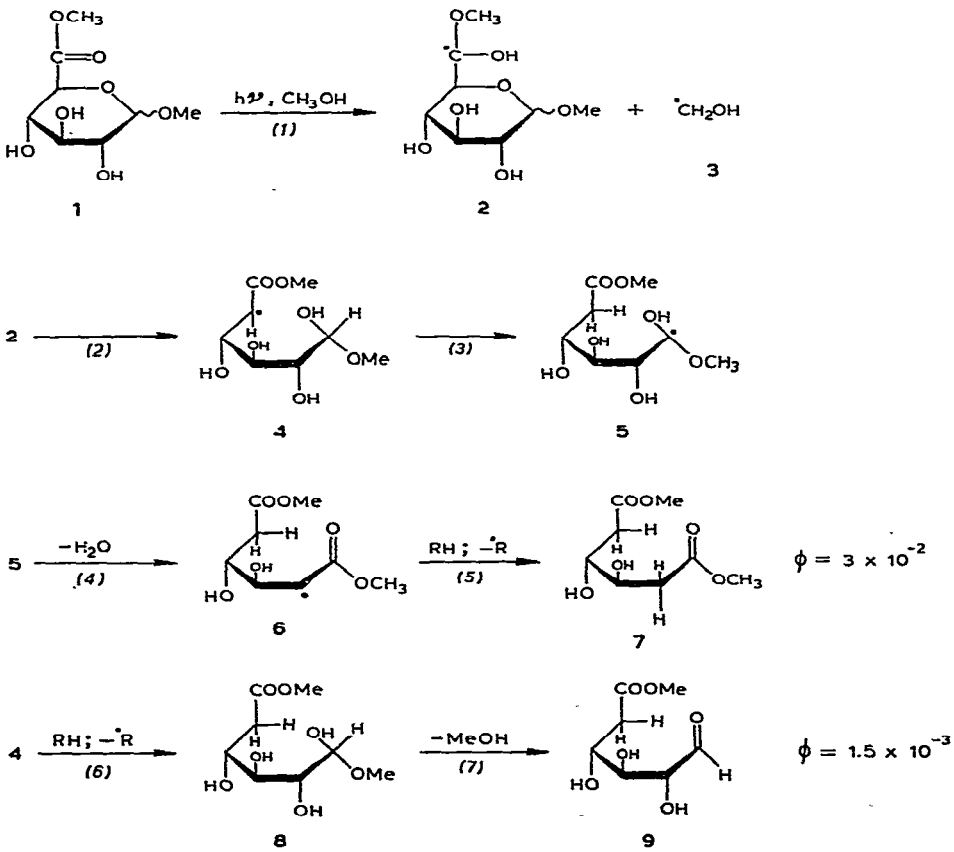
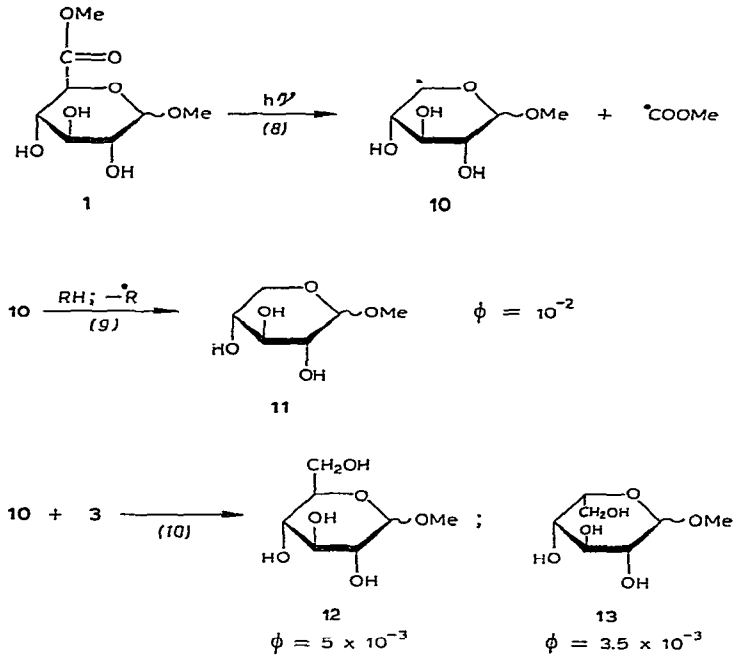
It has been shown by Kitagawa *et al.*[1] that the cleavage of glycosides of glucuronic acid esters with acid-sensitive aglycons, such as saponins, can be conveniently





carried out by photolysis. Although the method gives good results, the mechanistic routes still warrant elucidation. As the chromophore in these systems is the carbonyl function of the uronic ester, we have investigated the photolysis of methyl (methyl D-glucopyranosid)uronate (**1**, 10^{-2}M) in deoxygenated methanolic solutions as a model system. Products were identified by g.l.c.–m.s. and n.m.r. spectroscopy, and quantitatively determined by g.l.c. Quantum yields are given in the proposed reaction scheme.

All of the products can be rationalized by assuming that photoreduction[2] (reaction *1*) and a Norrish Type I process[3] (reaction *8*) are the primary photochemical steps. Norrish Type II processes are disfavoured for steric reasons.

Radical **2** from reaction *1* undergoes ring opening[4,5] (reaction *2*) to give radical **4**, which abstracts a hydrogen atom intramolecularly (*cf.* Refs. 6 and 7) to give **5** from which water is then eliminated[8]. The resulting radical (**6**) abstracts a hydrogen atom from the solvent to give dimethyl 2,5-dideoxy-D-*threo*-hexarate (**7**). The suggested mechanism was substantiated by photolysing **1** in CD_3OD. One deuterium atom was incorporated in one of the deoxy groups of **7**. Alternatively, radical **4** can also abstract a hydrogen atom from the solvent to give **8**, which eliminates methanol to give methyl 5-deoxy-D-*xylo*-hexuronate (**9**). In the experiments with CD_3OD, the ratio of **9** to **7** was strongly reduced (no mass spectrum of **9** obtainable). This is thought to be due to a marked isotope effect in reaction *6* which forces the reaction preferentially towards reaction *3*. Support for this interpretation was obtained by photolysing **1** in 2-propanol, which is a better hydrogen

donor. In this case, the ratio of **9** to **7** was increased by a factor of 25 compared to that in methanol.

The radical (**10**) resulting from cleavage between C-5 and C-6 (reaction *8*) either abstracts a hydrogen atom from the solvent (1 D incorporated on photolysis in CD_3OD) to give methyl D-xylopyranoside (**11**) or reacts with solvent radicals $\cdot CH_2OH$ to give methyl D-glucopyranoside (**12**) and methyl L-idopyranoside (**13**). Radical **10** is almost planar or readily inverts, and the $\cdot CH_2OH$ radicals can add from either side. For steric reasons, one mode is usually preferred (*cf.* Ref. 9). In the present case, this is reflected by the difference in ϕ (**12**) and ϕ (**13**). On photolysis in CD_3OD, the latter products have two deuterium atoms incorporated at C-6 (*cf.* the mass spectrum in Ref. 10). In the glycosides **11**, **12**, and **13**, the α to β ratio of the starting material was retained, thus indicating no preferential photolysis of either anomer. As carbon monoxide formation is observed, the alternative Norrish Type I process (C–O bond scission in the ester function) may also lead to radical **10**. The intermediate acyl radical is expected to rapidly eliminate carbon monoxide[11].

Aglycon elimination is only observed in the formation of product **9**. However, under preparative conditions using light intensities higher than those in our experiments, radicals **4** and **5** might also undergo combination reactions with other radicals present and thus preserve the labile hemiacetal group. Furthermore, under preparative conditions, **7** will be photolysed and is expected to eliminate the former aglycon group *via* a Norrish Type I reaction[3]. Thus, the primary steps in the photolysis of the saponins[1] may still proceed by routes similar to those depicted here in our model.

EXPERIMENTAL

Methyl (methyl D-glucopyranosid)uronate[11] (**1**) was purified by column chromatography. Vacuum drying gave a colourless, highly hygroscopic solid, ε (254 nm) = 6.5 $l.mol^{-1}.cm^{-1}$. G.l.c. and n.m.r. spectroscopy showed an anomeric mixture ($\alpha:\beta$ = 3.5). N.m.r. data (Me_2SO-d_6: δ 3.27 (s, α-OMe), 3.38 (s, β-OMe), and 3.64 (s, α- and β-COOMe).

Photolysis (λ 254 nm) was performed with a Hg low-pressure arc (Gräntzel, Karlsruhe) and a Vycor quartz filter which cuts off the 185-nm line. Light intensity was 1.1×10^{18} quanta (254 nm) min^{-1} per cell volume (2 ml).

Dimethyl 2,5-dideoxy-D-*threo*-hexarate (**7**) was isolated from preparative-scale photolysis by column chromatography (silica gel; acetone–ethyl acetate–water, 5:4:1), followed by recrystallisation from acetone–ether. The product had m.p. 89°. P.m.r. data (Me_2SO-d_6): δ 2.25 (q), 3.53 (s), 3.80 (m), and 4.84 (d, J 5 Hz). ^{13}C-n.m.r. data (D_2O): δ 40 (t), 54 (q), 74 (d), and 176 (s). I.r. data (CCl_4 film, KBr): 1733 cm^{-1}. The mass spectrum of the Me_3Si ether of **7** showed prominent ions at *m/e* 335 (M − 15; 2%), 319 (M − 31; 2%), and 175 (30%) (*m/e* 73; 100%). The mass spectrum of the Me_3Si derivative of a $NaBD_4$-reduced sample of **7** had prominent fragment ions at *m/e* 105 (100%) and 221 (25%), indicating[12] the Me_3Si ether of a 2,5-dideoxyhexitol-*1,1,6,6*-d_4.

Methyl D-xylopyranoside (**11**) and methyl D-glucopyranoside (**12**) were identified by g.l.c.–m.s. comparison with authentic material. The stereochemistry of methyl L-idopyranoside (**13**) is deduced from the mechanistic considerations (see above). Methyl 5-deoxy-D-*xylo*-hexuronate (**9**) was identified by g.l.c.–m.s. after reduction with $NaBD_4$ and trimethylsilylation. Principal fragment ions were at *m/e* 73 (100%), 103 (10%), 104 (10%), 105 (60%), 147 (15%), 206 (3%), 221 (20%), 238 (8%), 308 (4%), 323 (2%), and 335 (1%). The prominent ions *m/e* 217 (35%), 204, and 305 (1%) in the mass spectrum of unreduced, trimethylsilylated **9** indicated a furanoid ring[10].

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