Measurement of Ion Hydration by the Diffusion Method

By A. Hunyar

C. H. Hale and T. de Vries have recently reported[1] that the hydration of quaternary ammonium salts cannot be determined by the Nernst–Washburn method[2] because the reference substance as well as water is transported during electrolysis. This fact was previously demonstrated by T. Erdey-Gruz and A. Hunyar[3] using a modified form of the diffusion method developed by J. W. McBain and T. H. Liu.[4] They usually employed allyl alcohol of various concentrations as a reference substance and hydrochloric acid, potassium bromide, potassium chloride, lithium chloride, lithium acetate and tetramethylammonium chloride as electrolytes. They found that the concentration of the reference substance decreased, with one exception, in that part of the apparatus from which the electrolyte diffused and increased in that part into which it diffused.[5] The remarkable fact concerning these experiments was that the amount of allyl alcohol transported increased nearly linearly with the concentration of alcohol in the range 0.2 to 25% from 0.003 to 0.31 mole of allyl alcohol per mole of potassium chloride. The amount of alcohol transported decreased from 0.033 mole of allyl alcohol per mole of potassium chloride on the first day to 0.023 on the fourth day which was mathematically shown to be due to the back diffusion of the alcohol. The following results were obtained.

Electrolyte	Hydration numbers by Remy[6]	Mole of allyl alcohol per mole electrolyte
$LiC_2H_3O_2$	22.0	0.041
LiCl	15.6	.033
$N(CH_3)_4Cl$	7.6	.015
KCl	7.1	.031
KBr	6.2	.025
HCl	4.0	.005

Pogány[7] also observed that the electrolytes carried more reference substance than water, using the diffusion method. In the electrolysis of a solution of silver nitrate with pyridine as reference substance, Morgan and Kanolt[8] reported that a large proportion of the pyridine was combined with silver ions.

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[1] Hale and De Vries, This Journal, **70**, 2473 (1948).

[2] Washburn, *ibid.*, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

[3] Ph.D. Dissertation of A. Hunyar, Budapest, 1937.

[4] McBain and Liu, This Journal, **53**, 59 (1931).

[5] The exception was the case of arsenic trioxide as a reference substance with potassium chloride as electrolyte, when it was observed that more water than arsenic trioxide was transported. An average of 1.4 mole of water per mole of potassium chloride was carried.

[6] "Handbuch f. Exp. Phys.," Vol. XII, part 1, p. 293.

[7] Pogány, *Magyar Chém. Folyoirat*, **48**, 85 (1942); *C. A.*, **38**, 3186 (1942).

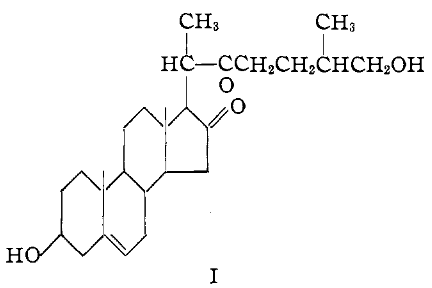
[8] Morgan and Kanolt, This Journal, **28**, 572 (1906).

Steroidal Sapogenins. III. 16-Alkylsapogenins[1]

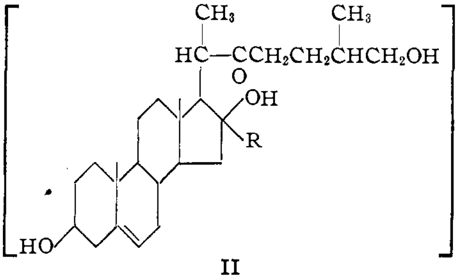
By St. Kaufmann and G. Rosenkranz

Through our recent work[1] it became evident that the two keto groups of the open-side-chain sapogenin, kryptogenin, possess different reactivity and that the conversion into sapogenins of the spiroketal form can easily be achieved as soon as the hydroxy group is introduced in the 16-position: we prepared[2] the 16-dihydrokryptogenin, a very unstable compound which can easily be transformed into diosgenin.

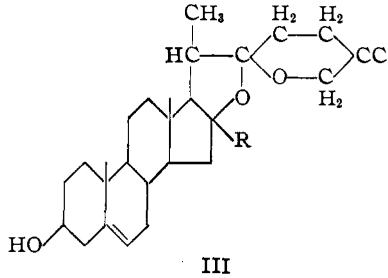
Based on this selective behavior of the 16-keto group we now reacted kryptogenin (I) with alkylmagnesium halides and obtained the respective 16-alkyldiosgenins (III) in good yield. The intermediate compound is very probably a 16-alkyl derivative of 16-dihydrokryptogenin (II)



I



II



III

The same reaction occurs with the esters of kryptogenin. If an excess of alkylmagnesium halide is used, the ester groups also react, thus yielding the free compounds.

In analogous manner, 5,6-dihydrokryptogenin or its esters can be transformed into the 16-alkyltigogenins. These latter compounds can be obtained also from the respective 16-alkyldiosgenins

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[1] For Paper II in this series see Rosenkranz, Kaufmann, Landa, Corona and Olalde, This Journal, **70**, 3518 (1948).

[2] Kaufmann and Rosenkranz, *ibid.*, **70**, 3502 (1948).