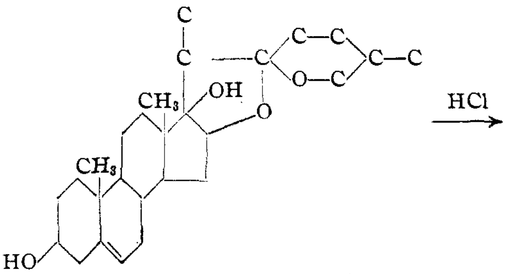
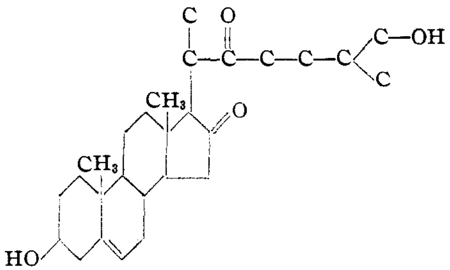
## STEROLS. CLV. SAPOGENINS. LXVII. PENNOGENIN, NOLOGENIN AND FESOGENIN, THREE NEW SAPOGENINS FROM *BETH* ROOT

*Sir:*

We have investigated the steroidal sapogenin fractions from *Beth* root collected at seven different localities during the past two years. One of these lots was obtained from S. B. Penick and Company. We have found that diosgenin accounts for 35–60% of the total steroidal sapogenin fractions. From the mother liquors of the crystalline diosgenin acetate was obtained kryptogenin acetate [Marker and co-workers, THIS JOURNAL, **65**, 739 (1943)], m. p. 154°, in 20–40% yields. Hydrolysis of the mother liquors from kryptogenin acetate gave a new steroidal sapogenin having the composition $C_{27}H_{42}O_4$, m. p. 247°, which we have named Pennogenin. *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8. Found: C, 74.9; H, 10.0. The yields of the latter varied from 10–20% of the total sapogenin fractions. Two of the oxygen atoms are present as hydroxyl groups, one of which acts with boiling acetic anhydride to form a monoacetate, m. p. 200°. *Anal.* Calcd. for $C_{29}H_{44}O_5$: C, 73.7; H, 9.4. Found: C, 73.6; H, 9.6. Pennogenin shows no ultraviolet absorption for a free carbonyl group. Prolonged treatment of pennogenin (I) with ethanolic hydrochloric acid gives kryptogenin (II). We propose structure I for pennogenin.



I. Pennogenin



II. Kryptogenin

In each of the sapogenin fractions isolated from the seven different sources of Beth root, the three above products accounted for over 85% of the total crystalline sterols.

The mother liquors from pennogenin, however, contain relatively smaller amounts of two new sapogenins, m. p. 265 and 180°, which we have named nologenin and fesogenin, respectively. Both give precipitates with alcoholic digitonin and give tests for unsaturation.

Nologenin, having the composition $C_{27}H_{44}O_5$, was isolated from the crude crystalline pennogenin fraction. *Anal.* Calcd. for $C_{27}H_{44}O_5$: C, 72.3; H, 9.8. Found: C, 72.3; H, 9.5. Boiling acetic anhydride formed a diacetate, m. p. 180°. *Anal.* Calcd. for $C_{31}H_{48}O_7$: C, 70.0; H, 9.1. Found: C, 70.0; H, 9.2. Although its solubility and melting point correspond to those of chlorogenin, the two compounds are readily differentiated by their analyses and the melting points of their acetates.

Fesogenin having the composition $C_{27}H_{40}O_3$ was isolated from the mother liquor of the crude crystalline pennogenin fraction. *Anal.* Calcd. for $C_{27}H_{40}O_3$: C, 78.6; H, 9.8. Found: C, 78.3; H, 9.8. Catalytic hydrogenation using palladium–barium sulfate catalyst gave dihydrofesogenin, m. p. 213°. *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 77.8; H, 10.2. Reduction with sodium in alcohol gave tetrahydro-fesogenin, m. p. 240°. *Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.7. Found: C, 77.6; H, 10.6. These reduction experiments indicate a conjugated system. The details of the isolation work and structure proof will be given in a forthcoming issue of THIS JOURNAL.

We thank Parke, Davis and Company for their help.

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## STEROLS. CLVI. SAPOGENINS. LXVIII. THE STEROIDAL SAPOGENIN FROM *BALANITES AEGYPTICA* (WALL.)

*Sir:*

Kon and Weller [*J. Chem. Soc.*, 800 (1939)] have reported the isolation of a new steroidal sapogenin, nitogenin, from the kernels of *Balanites aegyptica* (Wall.). Its properties have been described as follows: m. p. 201°, $[\alpha]_D$ −112° in chloroform, *Anal.* C, 77.6; H, 10.5; acetate,

m. p. 192°, *Anal.* C, 76.1; H, 10.0; benzoate, m. p. 229°, *Anal.* C, 78.2; H, 9.1. This material differed from tigogenin and sarsasapogenin by direct comparison. However, the authors failed to note its similarity to diosgenin. Thus, diosgenin isolated from *Dioscorea tokora* [Fujii and Matsukawa, *J. Pharm. Soc. Japan*, **56**, 408 (1936)] has the following properties: m. p. 200°, $[\alpha]^{19}_D$ $-119°$ in chloroform, *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2, H, 10.2.; acetate, m. p. 190°, *Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7.; benzoate, m. p. 237°, *Anal.* Calcd. for $C_{34}H_{46}O_4$: C, 78.7; H, 9.0.

We have obtained a sample of palm kernels identified for us as *Balanites aegyptica.* The sapogenin fraction contained diosgenin as its principal constituent. The identification was made by the melting point and mixed melting point determinations on the free genin, 206°; acetate, 200°; and benzoate, 238°. Catalytic reduction of its acetate gave tigogenin acetate, m. p. and mixed m. p., 202°. A mixture containing the latter and the original acetate melted 186°.

We thank Parke, Davis and Company for their help.

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## FURTHER REVISION OF THE CONSTANTS OF THE DEBYE-HÜCKEL THEORY

*Sir:*

In a recent note Stonehill and Berry[1] have published revised values for the constants $h$ and $g$ in the Debye–Hückel expression for the logarithm of the activity coefficient of a $z_1,z_2$-valent electrolyte in aqueous solution at 25°

$$\log_{10} \gamma = \frac{-hz_1z_2\sqrt{I}}{1 + ga\sqrt{I}} - \log_{10} (1 + 0.018\Sigma m_i)$$

On the basis of the physical constants tabulated by Childs[2] they find $h = 0.5103$ and $g = 0.3290 \times 10^8$. They indicate some of the possible implications of this change from the values $h = 0.5065$ (or 0.5056) and $g = 0.3287 \times 10^8$ (or $0.3288 \times 10^8$) based on the old values of the fundamental constants and used so widely by numerous authors.[3] The values of $h$ and $g$ established by Stonehill and Berry are, however, not final. The fundamental constants given by Birge[4] differ somewhat from, and supersede, those listed by Childs and used by Stonehill and Berry in their calculations. On the basis of the Birge constants $e = 4.8025 \times 10^{-10}$ e. s. u. (instead of Childs' $4.803 \times 10^{-10}$), $k = 1.38047 \times 10^{-16}$ erg/°C. (instead of $1.379 \times 10^{-16}$), $N = 6.0228 \times 10^{23}$ (instead of $6.028 \times 10^{23}$), $T_0 = 273.16$ (instead of 273.18) and on the basis of Wyman's[5] value 78.54 for the dielectric constant of water at 25° we find $h = 0.5091$ and $g = 0.3286 \times 10^8$. Calling $d$ and $t$ the ratios $D/78.54$ and $T/298.16$ we have, in general

$$h = \frac{0.5091}{(dt)^{3/2}} \text{ and } g = \frac{0.3286 \times 10^8}{(dt)^{1/2}}$$

The revised constant $l$ for the osmotic coefficient formula

$$1 - G = lz_1z_2\sqrt{I}\cdot\sigma(ga\sqrt{I})$$

is 0.3908 for water at 25° and, in general

$$l = 0.3908/(dt)^{3/2}$$

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(1) Stonehill and Berry, THIS JOURNAL, **64**, 2724 (1942).

(2) Childs, "Physical Constants," Methuen, London, 1939.

(3) On the basis of the constants tabulated by Fowler in his 'Statistical Mechanics" (Cambridge University Press, 1936) Van Rysselberghe and Eisenberg (THIS JOURNAL, **61**, 3030 (1939), **62**, 451 (1940)) and Eisenberg (Thesis, Stanford University, 1942) used the values $h = 0.5059$ and $g = 0.3287 \times 10^3$.

(4) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(5) Wyman, *Phys. Rev.*, **35**, 623 (1930).

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## CONSTANTS OF THE DEBYE-HÜCKEL THEORY

*Sir:*

In accordance with the revised constants of Birge quoted in the preceding Communication of Dr. Van Rysselberghe, the equations of Scatchard and Epstein[1] for the Debye–Hückel limiting-law expressions in terms of concentrations in moles per kilogram of water should also be revised to give

$$\ln \gamma_k/z_k^2 \sqrt{\mu} = 1.1244 \, [1 + 0.15471 \, (t/100) + 0.03569 \, (t/100)^2 + 0.02389 \, (t/100)^3]$$

$$\ln \gamma_k/z_k^2\kappa = 3.470 \times 10^{-8} \, [1 + 0.10194 \, (t/100) + 0.04269 \, (t/100)^2 + 0.00976 \, (t/100)^3]$$

$$\kappa/\sqrt{\mu} = 0.3240 \times 10^8 \, [1 + 0.05217 \, (t/100) - 0.00916 \, (t/100)^2 + 0.00888 \, (t/100)^3]$$

in which $\gamma_k$ is the ratio of the activity of the $k$'th ion species to its molality, $z_k$ is its valence, $t$ the centigrade temperature, $\mu$ the ionic strength,

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(1) G. Scatchard and L. F. Epstein, *Chem. Rev.*, **30**, 211 (1942).