QUANTUM EFFECTS IN COMPRESSED LIQUID HYDROGEN

Sir:

Johnston, Keller and Friedman[1] recently have published measurements of the compressibility of liquid hydrogen and shown that there is a marked discrepancy between their experimental results and the classical Lennard-Jones and Devonshire[2] (LJD) isotherms. They ascribed this disagreement to the lack of sphericity of the hydrogen molecules and to quantum effects. The purpose of this note is to show that the second factor is probably the more important of the two.

Quantum corrections to the LJD theory were worked out by de Boer and Lunbeck[3] and by the present author,[4] and it has been shown[5] that they adequately explain the failure of the classical LJD theory for compressed gaseous hydrogen and deuterium. It is not difficult to carry out similar calculations for liquid hydrogen and derive the pressure corrections listed in Table I.

In Table I, T is the absolute temperature, P is the pressure and V is the molar volume of the gas; k is Boltzmann's constant and R is the gas constant. V_0 ($= N\sigma^3$) and ϵ are quantities characteristic of the potential field between hydrogen molecules: they have been taken from the tables of de Boer and Lunbeck.[3] The quantum correction was derived from equations (6), (5) and (2) of reference 4, the series (2) being summed numerically.

Figure 1 compares the classical and quantal isotherms with the experimental results of Johnston, Keller and Friedman.[1] It is apparent that the quantum correction removes much of the discrepancy between the predictions of the LJD theory and the actual behavior of liquid hydrogen.

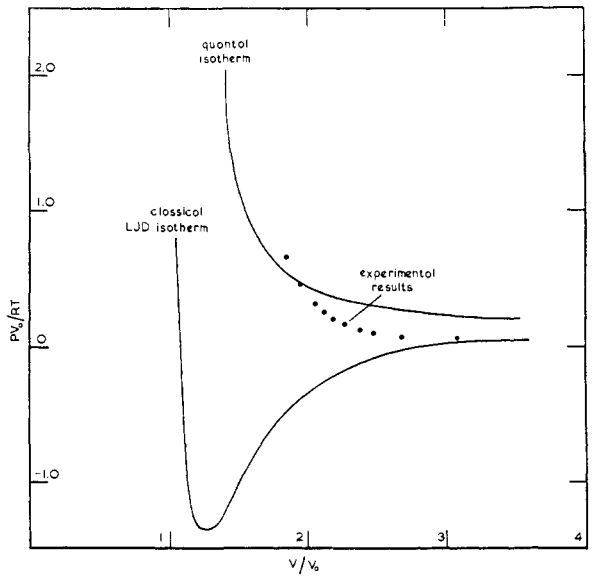

Fig. 1.—Isotherms of liquid hydrogen at 32.58° K.

(1) H. L. Johnston, K. E. Keller and A. S. Friedman, THIS JOURNAL, **76**, 1482 (1954).

(2) J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)*, **A163**, 53 (1937).

(3) J. de Boer and R. J. Lunbeck, *Physica*, **14**, 520 (1948).

(4) S. D. Hamann, *Trans. Faraday Soc.*, **48**, 303 (1952).

(5) H. G. David and S. D. Hamann, *ibid.*, **49**, 711 (1953).

TABLE I

THEORETICAL PRESSURE OF LIQUID HYDROGEN AT 32.58°K.
Reduced temperature $kT/\epsilon = 0.88$

Reduced volume, V/V_0	Reduced pressure PV_0/RT: Classical LJD theory[a]	Quantum correction	Total
1.2728	−1.34	+5.52	+4.18
1.4142	−1.20	+3.16	+1.96
1.5556	−0.93	+1.93	+1.00
1.7678	− .57	+1.19	+0.62
1.9799	− .34	+0.80	+ .46
2.4749	− .094	+ .425	+ .331
3.5355	+ .041	+ .186	+ .227
4.2426	+ .066	+ .125	+ .191

[a] From the tables of Wentorf, Buehler, Hirschfelder and Curtiss.[6]

(6) R. H. Wentorf, R. J. Buehler, J. O. Hirschfelder and C. F. Curtiss, *J. Chem. Phys.*, **18**, 1484 (1950).

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RECEIVED JULY 19, 1954

CRYSTALLIZATION AND PROPERTIES OF A GLYCOPROTEIN ISOLATED FROM HUMAN PLASMA

Sir:

A glycoprotein has been isolated and crystallized from Fraction III-O[1] of pooled normal human plasma. This is thought to be one of the lipid-poor euglobulins described by Oncley, Scatchard and Brown.[2] Freshly prepared Fr III-O paste is dialyzed at −5° for 24 hours against thirty volumes of a solution of 1.65 M sodium chloride and 0.004 M phosphate buffer at pH 7.0. The dialysis is continued for an additional 24 hours against fresh solution. This procedure removes the alcohol and brings the paste into solution at a solvent density of 1.06. To sediment the glycoprotein, the III-O solution is ultracentrifuged for 18 hours at 97,720 G. The floating lipoproteins are sliced from the top of the tube by means of a sharp blade in a rigid holder and the material in solution is discarded.

The glycoprotein pellet thus obtained is about 85% homogeneous electrophoretically. The material precipitating between 30 and 40% saturation with ammonium sulfate solution is 92% pure. Dissolving the pellet in a solvent of density 1.21 (1.64 mole of sodium chloride and 1.79 mole of potassium bromide in one liter of distilled water), ultracentrifuging as previously, produces a pellet 97% homogeneous electrophoretically and about 80% ultracentrifugally. The glycoprotein can be crystallized at this point. Repeating the procedure twice yields material essentially homogeneous in the ultracentrifuge.

Crystallization method: a 5% solution in 0.012 M acetate buffer, pH 5.4 is filtered through a medium sintered glass filter and dialyzed at 0° against a solution of 0.15 M sodium chloride and of 0.00012 M acetate buffer at pH 5.4. Water is added gradually to the dialyzate for two weeks.

(1) J. L. Oncley, M. Melin, D. A. Richert, J. W. Cameron and P. M. Gross, Jr., THIS JOURNAL, **71**, 541 (1949).

(2) J. L. Oncley, G. Scatchard and A. Brown, *J. Phys. Colloid Chem.*, **51**, 184 (1947).

Crystals, six-sided rods, appear when the sodium chloride concentration is 0.105 *M*.

TABLE I

CONSTANTS FOR THE GLYCOPROTEIN

Hexose/protein (protein is taken as nitrogen × 6.25)	0.053
Hexosamine/protein	0.038
$E^{1\%}_{1\text{ cm.}}$ at 277 mμ	11.1
Biuret color of protein portion (albumin = 1.00)	0.98
Sedimentation constant (2% soln)	14.6 Svedbergs
Electrophoretic mobility barbiturate *p*H 8.6, Γ/2 0.1	-3.92×10^{-5} cm.²/volt sec.

A suspension of crystals in saline was dried and weighed; 93% was composed of protein, carbohydrate and calculated salt, a further indication that the crystals are protein in nature.

The crystallized glycoprotein is ultracentrifugally homogeneous although the sedimentation diagram indicates slight denaturation during solution. Marked ultracentrifugal changes consistent with denaturation occur if the crystals are suspended in distilled water. Freezing and thawing cause the formation of two new well-defined ultracentrifugal components. In a typical experiment at a protein concentration of 2%, 9% of a component of $S_{20,w}$ = 21.4 and 3% of a component of $S_{20,w}$ = 9.8 were found.

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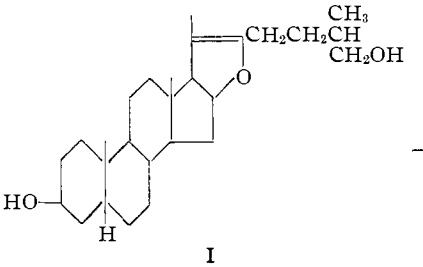
RECEIVED JUNE 21, 1954

THE TRANSFORMATION OF PSEUDOSAPOGENINS TO STEROID ALKALOIDS[1]

Sir:

In pursuit of studies directed toward the synthesis of steroid alkaloids of skeletal formulations characteristic of natural products,[2] pseudosapogenins have been investigated as starting materials. Pseudosarsasapogenin, I,[3,4] has been converted, following treatment with *p*-toluenesulfonyl chloride and pyridine, to an iodo derivative, m.p. 60–62° [*Anal.*[5] Calcd. for $C_{27}H_{43}O_2I$: C, 61.59; H, 8.23; I, 24.12. Found: C, 61.38; H, 8.42; I, 24.25] which has been transformed with potassium phthalimide in dimethylformamide to the C.27 phthalimido derivative II, m.p. 187–188° [*Anal.* Calcd. for $C_{35}H_{47}NO_4$: C, 77.02; H, 8.68; N, 2.57. Found: C, 76.71; H, 8.64; N, 2.81]. Cleavage with hydrazine and subsequent treatment with mineral acid has afforded an alkaloid III, m.p. 221–223°, $[\alpha]^{25}D$ −17.4° (methanol) [*Anal.* Calcd. for $C_{27}H_{45}NO_2$: C, 78.02; H, 10.91; N, 3.37. Found: C, 78.23; H, 10.85; N, 3.25].



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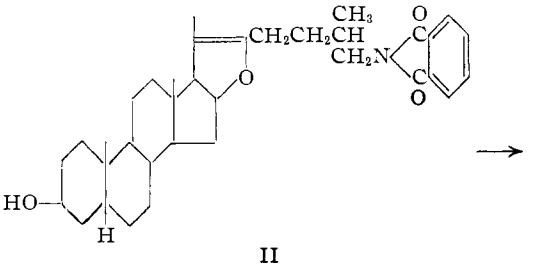
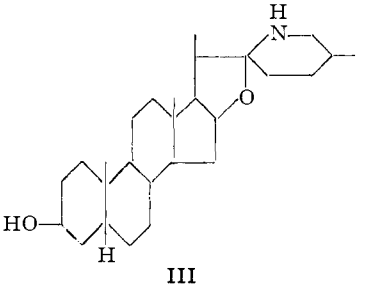


II



III

A parallel approach employing pseudodiosgenin has afforded solasodine. Although the singular lability of pseudodiosgenin and of its derivatives has, to the present, compromised repeated attempts to isolate and fully characterize the intermediates postulated for the sequence, it has been possible to transform pseudodiosgenin to solasodine as a continuous process in over-all yields of the order of ten per cent. Pseudodiosgenin-3-acetate-27-butyrate, m.p. 117–118° [*Anal.* Calcd. for $C_{33}H_{50}O_5$: C, 75.24; H, 9.57. Found: C, 75.49; H, 9.66] (from diosgenin acetate and refluxing butyric anhydride) and pseudodiosgenin dibutyrate, m.p. 78–79°, $[\alpha]^{26}D$ −16.8° (methanol) [*Anal.* Calcd. for $C_{35}H_{54}O_5$: C, 75.77; H, 9.81. Found: C, 75.60; H, 9.61] (from diosgenin or from pseudodiosgenin and refluxing butyric anhydride) on alkaline hydrolysis at 25° have yielded pseudodiosgenin, m.p. 161–162°, which, on successive treatment with *p*-toluenesulfonyl chloride in pyridine, sodium iodide in diethyl ketone, potassium phthalimide in dimethylformamide, and hydrazine in ethanol, has afforded solasodine, m.p. 200–201°, $[\alpha]^{25}D$ −118° (chloroform) [*Anal.* Calcd. for $C_{27}H_{43}NO_2$: C, 78.40; H, 10.48; N, 3.39. Found: C, 77.36; H, 10.52; N, 3.42] mixed melting point[6]

(1) Supported in part by the United States Public Health Service and the Eugene Higgins Trust of Harvard University.

(2) F. C. Uhle, THIS JOURNAL, **73**, 883 (1951); **75**, 2280 (1953).

(3) R. E. Marker and E. Rohrmann, *ibid.*, **62**, 519 (1940).

(4) The author is indebted to Dr. James A. Moore, Parke Davis and Company, Detroit, Michigan, and to S. B. Penick and Company, New York, N. Y., for quantities of sarsasapogenin and of diosgenin acetate.

(5) Microanalyses and spectroscopic determinations by Dr. S. M. Nagy and associates of the Massachusetts Institute of Technology, Cambridge, Massachusetts.

(6) The author is indebted to Prof. L. H. Briggs, Auckland University College, Auckland, New Zealand, and to Dr. Yoshio Sato of the National Institutes of Health, Bethesda, Maryland, for authentic samples of solasodine.