residues. To examine this point further, we contemplate performing complete combustions of these products.

We are glad to acknowledge our indebtedness to Dr. J. F. Snell for the facilities of these laboratories and to Dr. Darol K. Froman for his kind assistance.

DEPARTMENT OF CHEMISTRY
MACDONALD COLLEGE
MCGILL UNIVERSITY, CANADA
W. W. STEWART
R. HOLCOMB

RECEIVED APRIL 21, 1934

THE HEAT CAPACITIES OF CRYSTALLINE, GLASSY AND UNDERCOOLED LIQUID GLUCOSE

Sir:

The heat capacities of glucose in the crystalline α-form (Pfanstiehl Chemical Co.) and in the undercooled glassy and liquid condition have been measured with a "radiation" calorimeter, described previously by Thomas and Parks [*J. Phys. Chem.*, **35,** 2091 (1931)]. The specific heats thereby obtained, expressed in calories per gram, are represented graphically by Curves 1, 2 and 3 in the accompanying figure. Curve 1 is for the α crystals and conforms closely to the linear equation $C_p = 0.270 + 0.00092t$. These crystals decomposed slightly when heated slowly up to the melting point. A measurement of their heat of fusion gave 41.7 cal./g. at about 141°. Curve 2 was obtained on heating undercooled liquid glucose, at the rate of about 10° per hour, from the condition of a hard, brittle glass to that of a highly viscous liquid ($\eta = 10^8$ poises at 48.5°). It shows a large maximum or "hump" between 28 and 38°. Conversely, Curve 3 was obtained while this glucose sample was similarly cooling from 45 to 10° and in this case no hump appears, although the total energy changes represented under Curves 2 and 3 are approximately the same. Similar curves have been found with B_2O_3 glass.

In an earlier investigation Parks, Huffman and Cattoir [*J. Phys. Chem.*, **32,** 1366 (1928)] have measured the heat capacities of glassy and liquid glucose from −180 to +70°. Curve 4 represents their results within the temperature range of the present study. They used an aneroid calorimeter and the Nernst method, which involved the introduction of discontinuous increments of energy sufficient to raise the temperature at the rate of about 3° per hour. No hump appears in this curve but there is a 60% rise in the heat capacity between 5 and 15°.

The marked differences between Curves 2 and 4 are due to two factors: (1) the use of different samples of glucose glass, with perhaps a few tenths of one per cent. of water (as an impurity) in the material with Curve 4, and (2) the employment of very different methods in heating these samples in this transition range within which the hard glass is transformed into a pasty liquid.

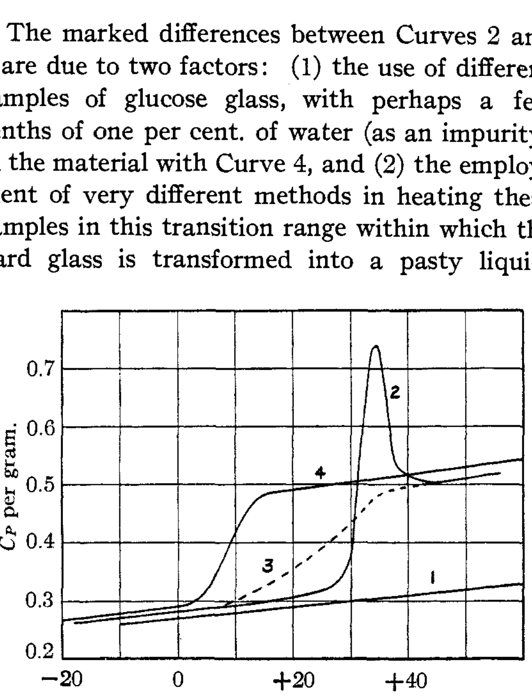

Fig. 1.

In our judgment the second factor is the more important, at least in determining the shape of the curves. In the case of Curve 4 the temperature interval from 5 to 40° was traversed discontinuously in a period of over forty-eight hours; with Curve 2 it was traversed by a continuous heating process within four hours. Curve 4 undoubtedly represents a much closer approach to a true equilibrium condition, although probably no process carried on with a glassy material within finite time can be regarded as involving complete equilibrium. Above 40° the 4% difference between Curves 2 and 4 should probably be attributed to experimental errors, as each method at this temperature may have involved absolute systematic errors of 2 or 3%.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIF.
GEORGE S. PARKS
S. BENSON THOMAS

RECEIVED APRIL 24, 1934

SEPARATION OF DEXTRO AND INACTIVE LUPANINES

Sir:

No convenient method has been reported for separating the mixture of optically isomeric alkaloids derived from *Lupinus albus*. Soldaini [*Arch. Pharm.*, **231** 321, (1893)], and Davis [*ibid.*, **235,** 200 (1897)] accomplished the separation by fractional crystallization of the hydrochlorides. A simpler procedure has now been developed.

The mixed alkaloids extracted from white lupine seeds were freed from residual solvent and impurities by vacuum distillation. Both forms distil at the same temperature, 220–226° at 12 mm. The distillate had n^{24}_{D} 1.5400; $[\alpha]^{25}_{D}$ 32.02 in alcohol (indicating 38% of *d*-lupanine). It solidified on standing, softened at 40°, became fluid at 67° and was completely melted at 81°; 105 g. was extracted with four 75-cc. portions of warm petroleum ether [Soldaini, *op. cit.*, states that *dl*-lupanine is insoluble in this solvent]. The undissolved material was dissolved in warm acetone and on cooling the solution deposited 20 g. of rhombic prisms, m. p. 98°, $[\alpha]_{D}$ 1.14° at 27° in alcohol. These were recrystallized from acetone and yielded optically inactive colorless prisms of *dl*-lupanine, m. p. 98°. Further crops were obtained from the mother liquors. The last mother liquor contained much *d*-lupanine which was recovered by the method used for the petroleum ether soluble fraction.

The petroleum ether solution was cooled and then deposited 7.5 g. of long needles melting above 90°. The solution was evaporated and left 31 g. of sirupy base that gradually crystallized; in water $[\alpha]^{25}_{D}$ 56.86° (indicating 67.4% of *d*-lupanine). The *d*-base was purified by adapting the method of Ingersoll [THIS JOURNAL, **47,** 1168 (1925)], which has been used successfully by Clemo, Raper and Tenniswood [*J. Chem. Soc.*, 429 (1931)] to resolve *dl*-lupanine: 24.3 g. of the mixed alkaloids in 25 cc. of acetone was added to a mixture of 23 g. of *d*-camphorsulfonic acid and 25 cc. of acetone. Heat was evolved and the whole went into solution. On cooling a good yield of crystals was obtained which when recrystallized from acetone yielded 23.5 g. of *d*-lupanine camphorsulfonate, m. p. 116–8°, $[\alpha]^{29}_{D}$ 44.76° (4.184 g. in acetone). The whole was dissolved in 35 cc. of water, and 7.7 g. of potassium iodide (1 mole) was added. Small needle crystals of the hydriodide were formed immediately, m. p. 183–184°, $[\alpha]^{25}_{D}$ 43.31° (5.084 g. in water). These dissolved in water, made alkaline with sodium hydroxide and extracted with chloroform yielded *d*-lupanine as a sirup that slowly crystallized. It distilled between 190 and 195° at 3 mm. The fluid distillate had n^{24}_{D} 1.5444 and, in alcohol, $[\alpha]^{25}_{D}$ 84.35°, $l = 2$, $c = 4.776$, $a = 7.782°$.

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.
JAMES FITTON COUCH

RECEIVED APRIL 30, 1934

THE DEHYDROGENATION OF GITOGENIN

Sir:

The authors have recently studied the dehydrogenation of sarsasapogenin with selenium, a report of which is now in press [*Journal of Biological Chemistry*]. The reaction has yielded a low boiling fraction from which a semicarbazone was obtained which melted at 143–144° and analyzed as the derivative of a ketone $C_8H_{16}O$. This melting point does not agree with that (152°) reported for the same material by Ruzicka and van Veen [*Z. physiol. Chem.*, **184,** 69 (1929)] who concluded that it is the derivative of methyl isohexyl ketone. Through the kindness of Prof. I. M. Heilbron, we have obtained a sample of the semicarbazone of methyl isohexyl ketone (m. p. 152°) which, when mixed with our semicarbazone, melted at 130–133° after preliminary softening. The identity of this ketone is under further investigation. In addition, from the higher boiling fractions a crystalline hydrocarbon mixture was obtained which yielded after repeated fractionation by the triangle scheme an apparently homogeneous hydrocarbon of melting point 123.5–124°. This at once suggested identity with methyl-cyclopentanophenanthrene (Diels' hydrocarbon, $C_{18}H_{16}$). This conclusion was strengthened by the preparation of the trinitrobenzene and trinitrotoluene addition products.

We have since made a parallel study of the dehydrogenation of the digitalis sapogenin, gitogenin, with similar results. From the low boiling fraction of the reaction mixture the same semicarbazone was obtained which melted at 144.5–145°. In addition, a crystalline hydrocarbon resulted which after extensive fractionation gave a substance which melted at 123.5–124° and showed no depression when mixed with Diels' hydrocarbon. For confirmation of identity a study of its derivatives is in progress.

It would appear, therefore, in so far as the formation of Diels' hydrocarbon, $C_{18}H_{16}$, may be considered a characteristic of the sterol ring system, that sarsasapogenin and the digitalis sapogenins as well as the cardiac aglucones are alicylic