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THE THIXOTROPY OF HEATHER HONEY

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The use of the viscometer for testing the purity of honey was introduced in 1911 by Fellenberg (4), who tested honeys mixed with water in an Ostwald viscometer.   Eisenschitz (3) has shown that honey mixed with water behaves as a normal viscous liquid.   It is known, however, that some undiluted honeys, even when not granulated, show abnormal viscous behavior (6), and de Boer and Kniphorst (1) have shown that stirred heather honey (from *Calluna vulgaris*) increases its viscosity gradually on standing. The rate at which this rise in viscosity takes place depends on the temperature, passing through a minimum at about 15°C., but even at this temperature, the viscosity (as measured by the time of outflow per gram from a Holde viscometer)[1] increases by many fold within twenty-four hours. On stirring, the viscosity returns to somewhere near its original value. This phenomenon is described by de Boer and Kniphorst as "thixotropy," but since it is not known how far this is really similar to the reversible sol-gel transformations to which the term thixotropy was originally applied, it is of interest to investigate further the viscous and rigid properties of the sol and gel forms.   No information seems to be available, for example, as to whether the stirred honey is a true fluid, which on standing sets into a rigid gel; whether the setting is caused by a rise in viscosity only; or whether both sol and gel forms show rigid properties.   Moreover, the phenomenon has a practical interest, since heather honey, by reason of its gelatinous character, holds its water in a different way from other honeys. Ordinary honey containing more than about 20 per cent of water (due to either immaturity or dilution) tends to ferment, whereas heather honey, since some of its water is held in an immobilized condition, does not do so until a considerably higher moisture content is reached.   The term "heather honey" is used to describe any honey derived largely from the nectar of *Calluna vulgaris*, *Erica cinerea*,[2] and allied species.   However, in many cases heather honeys are not obtained from a pure heather source,

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[1] For a description of this instrument see Lunge-Berl Chemische Technologische Untersuchungen, 7th edition, Vol. III, p. 461.

[2] Added January, 1935: It now appears probable that honeys derived from *Erica* alone are not thixotropic.

samples showing a range of properties between those of a honey obtained entirely from heather on the one hand, and of an ordinary non-thixotropic honey on the other. A method of assessing the extent to which a given sample showed the gelatinous and thixotropic properties of a heather honey would be of value in deciding whether an apparently excessive moisture content would be likely to lead to subsequent spoiling due to fermentation.

THE GEL FORM

To investigate the properties of the gel form, a ball viscometer was used. As a preliminary experiment, in view of the fact that only comparatively small samples were available, and that viscometer vessels could not, therefore, be very large compared with the size of the balls, the effect of wall-correction on the viscosity measurements on a normal liquid (Lyle's Golden Syrup) was tested.

TABLE 1

Rate of fall of balls through Lyle's Golden Syrup

DIAMETER OF BALL	TIME	$\dfrac{\text{VELOCITY}}{\text{DIAMETER}^2}$
inches	*seconds*	*arbitrary units*
1/2	34.5	0.116
5/16	52.3	0.194
1/4	65.0	0.247
7/32	81.5	0.256
3/16	98.5	0.291
5/32	126.2	0.329
1/8	175.0	0.356

A Nessler tube of internal diameter 3.1 cm., having marks etched at a distance of 6 cm. apart, was filled with syrup, and left to stand overnight. On the following morning, a number of steel balls were dropped through the liquid, the time in seconds taken to fall between the marks being recorded.

The balls are not small compared with the size of the tube, and the results given in table 1 show that the rate of fall is by no means proportional to the square of the diameter of the ball.

Although various corrections have been proposed to allow for such errors (5), it seemed more satisfactory to eliminate differences in the error by using two balls of different size, falling in vessels whose diameters bear an approximately constant ratio to the diameters of the balls.[3]

For this purpose, two glass cylinders were chosen, A having a diameter of 3.4 cm., and B a diameter of 4.8 cm. Into A were dropped balls of

[3] I am indebted to Dr. R. K. Schofield for suggesting this arrangement.

diameter 0.80 cm.($\frac{5}{16}$ in.), and into B balls of diameter 1.11 cm. ($\frac{7}{16}$ in.). For a true fluid, in which the viscosity is independent of shearing stress, the times taken for the balls to fall between the marks (5 cm. apart in each case) should bear a ratio equal to the ratio of the squares of their diameters.[4] Moreover, for a true fluid, the rate of the fall should be unaffected by stirring.

As a first experiment, balls were timed to fall through a sample of Lyle's Golden Syrup (a different sample from that used in the earlier experiment). Immediately after the test, a perforated metal disk was forced twice up and down through the syrup so as to cause a thorough stirring, and the test was repeated.

The test was repeated exactly with a sample of heather honey which had been left in the viscometer vessels overnight. It is clear from table 2 that whereas syrup has a viscosity which is reasonably independent of

TABLE 2

Viscosity of Lyle's Golden Syrup and heather honey

FLUID	VELOCITY IN CM. PER SECOND		VELOCITY/D^2	
	A	B	A	B
Lyle's Golden Syrup				
Before stirring........................	0.108	0.217	0.171	0.176
After stirring........................	0.110	0.216	0.175	0.176
Heather honey				
Before stirring........................	0.0475	0.137	0.076	0.112
After stirring........................	0.395	0.770	0.625	0.625

Two heather honeys were used in these experiments, designated X and Y. The experiments were performed at room temperature, 15°C.

both stress and stirring, heather honey shows a variable viscosity in its unstirred state, and that its viscosity falls enormously after stirring.

[4] As a first approximation, to account for the effect of the walls of the containing tube (which is assumed to be infinitely long) Ladenburg (Ann. Physik **22**, 287 (1907)) has proposed the introduction of a term into the denominator of the Stokes equation, which then reads:

$$\eta = \frac{2r^2 \, (\rho - \rho') \, g}{9v \, (1 + Ar/R)}$$

where r is the radius of the sphere
  R is the radius of the tube
  ρ is the density of the sphere
  ρ' is the density of the medium
  v is the velocity of the fall
  η is the viscosity, and
  A is a pure number.

Since the correction term $(1 + Ar/R)$ does not involve viscosity, the times of

To find whether this "gel" shows any marked yield value (i.e., whether the viscosity becomes practically infinite for very small stresses (cf. Scott Blair (9)), a very small ball (diameter ⅛ in.) was placed just below the surface of a sample of heather honey (Y). After some hours, it was clear that the ball had fallen appreciably; thus, although the viscosity is very high for such small stresses, it is unlikely that there is any sharp yield value for the gel.

THE SOL FORM

To find out whether the thoroughly stirred honey (the sol) behaves as a true fluid,[5] a sample of Y was stirred in the manner described above, and tested in the Rothamsted plastometer. This instrument has already been described (2, 8), and it will suffice to say that in it the material is forced by compressed air through a capillary tube of known dimensions under varying pressures, the amount of flow per second being recorded for each pressure. The plastometer thermostat was set first at 15°C., and, for a second experiment at 30°C. At the latter temperature, two different capillary tubes having radii of 0.088 cm. (No. II) and 0.048 cm. (No. IV) were used. Both tubes were 12.25 cm. in length.

By plotting stress[6] $(PR/2L)$ against velocity gradient $(4V/\pi R^3)$, curves are obtained which should be independent of the capillary dimensions, provided that: (1) each element of the material moves in a straight line parallel to the tube walls; (2) the material in contact with the wall is at rest with respect to it; and (3) the velocity gradient has a unique value for each value of shearing stress (cf. Schofield (7)). For true fluids the curves are linear, and pass through the origin.

It has been shown (8) that for certain pastes, the second and third conditions above do not hold, owing to anomalous flow near the tube walls. Moreover many materials, although obeying these three conditions, show a decrease in viscosity as stress increases, giving either a curvilinear flow-

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fall for a given tube and sphere remain proportional to the viscosities. Moreover, since in the above experiment the ratio r/R is the same in both cases, it is true to say that in so far as Ladenburg's approximations are applicable, the times of fall for the two balls will bear a ratio equal to the ratios of the squares of their diameters. Corrections due to the effect of the end of the tube (which cannot be regarded as anything like infinitely long in practice) are not large, and may be neglected for the purpose of the above experiments.

For a further discussion on this subject see Hatschek's Viscosity of Liquids, p. 33 (G. Bell and Sons, Ltd., London, 1928), and Barr's Viscometry, p. 171 (Humphrey Milton, London, 1931).

[5] Paine, Gertler, and Lothrop have already shown that certain (non-thixotropic) honeys show a slight fall in viscosity with increasing stress. A Bingham-Green plastometer was used.

[6] P is the pressure, R is the tube radius, L is the tube length, and V is the flow in cubic centimeters per second.

curve, or a curve which, although straight at high stresses, does not extra-polate to the origin (6).

It is clear from figure 1 that the sample of stirred heather honey (sol) shows no appreciable anomaly of the first type, but that, although ap-proximating closely to a true fluid (especially at 30°C.), there is a small but significant tendency for viscosity to rise at low stresses (though this is not great enough to be observed in the experiment shown in table 2).

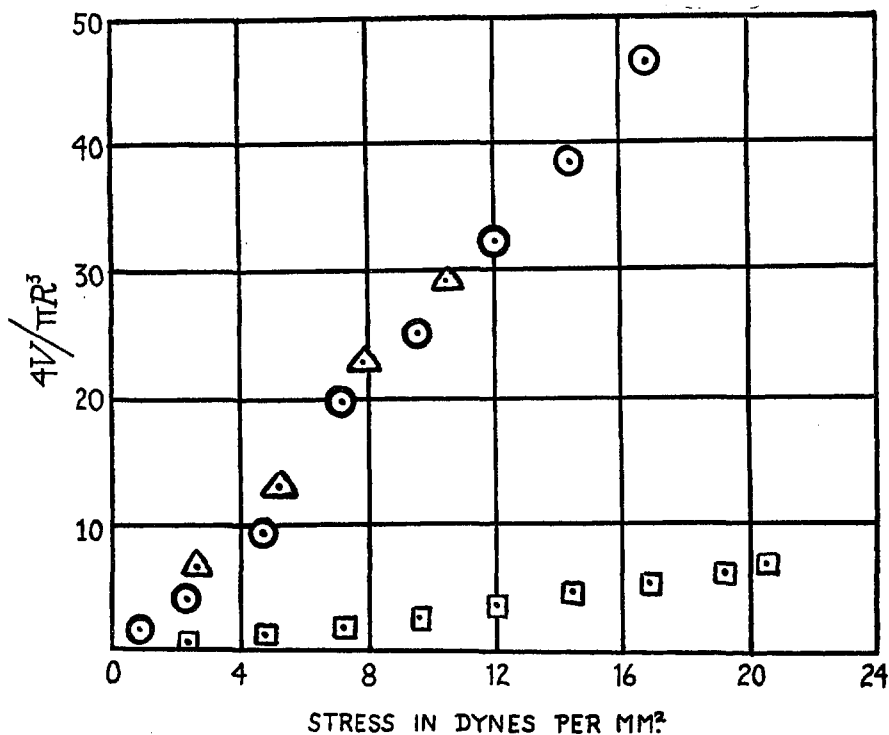There is no evidence of a sharp yield value.

FIG. 1. FLOW CURVES FOR HEATHER HONEY

⊙ Capillary II, 30°C.   △ Capillary IV, 30°C.   ⊡ Capillary II, 15°C.

At 30°C. sample Y shows a viscosity at high stresses of about 37 c.g.s. units, and at 15°C. of approximately 300 c.g.s., though at 15°C. it is not certain that all thixotropic structure was really destroyed by shearing. Such a high viscosity brings the experiment rather near the limits of applicability of the plastometer.

DISCUSSION

Heather honey "gel" shows "rigid" properties in the sense that at low stresses, rapidly applied, the viscosity of the system is so high that it may

be said to behave as an elastic solid, but there is no marked yield value— i.e., the elastic limit is not sharp. The change which takes place when the gel is broken up by stirring is a continuous one, involving a fall in viscosity and an increasing approximation to a truly fluid condition, but even a vigorously stirred sample shows signs of viscosity increase at very small stresses. The data are not adequate to specify just how sharp this change in viscosity may be, but there is certainly no well-defined yield value. A semiquantitative measure of thixotropy may be obtained by timing the fall of a steel ball through a sample of honey which has been left to stand overnight, disintegrating the gel by stirring with a perforated metal disk, and then immediately timing a second ball of the same size. Under fixed conditions, the ratios of the times of fall for heather honey before and after stirring show values of from about 5 to 200,[7] as compared with unity for Golden Syrup, and approximately unity for ordinary clover honey. If standardized conditions of temperature, size of vessel and balls, etc., are used, this should prove a useful test for deciding whether a sample is to be rejected on account of high moisture content, which in a normal honey would be an indication of "unripeness" and might lead to its subsequent spoiling by fermentation, or whether it is to be excused on the ground of its heather origin.

SUMMARY

Experiments are described on the behavior of heather honey under shearing, both in its undisturbed ("gel") and stirred ("sol") forms. In both cases, the viscosity increased at low stresses, but in neither case was there found any sharp elastic limit (yield value). The sol form showed (considering its very high viscosity) only a very small deviation from truly fluid behavior.

A simple viscometric test is described to characterize honeys having thixotropic properties. This test should prove of use in deciding whether excess water in a honey is caused by unripeness, or is natural, owing to its heather origin.

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[7] Not many samples have yet been tested, and it is possible that further tests will show a still larger range of values.

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