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HONEY

A COMPREHENSIVE SURVEY

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CHAPTER 6

PHYSICAL CHARACTERISTICS OF HONEY

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*Thence there flows
Nectar of clearest amber, redolent
Of every flowery scent
That the warm wind upgathers as he goes.*

MARTIN ARMSTRONG,
COLLECTED POEMS (1931)

6.1 INTRODUCTION

From the physical viewpoint, honey as extracted from the comb is an aqueous dispersion of material covering a wide range of particle size—from inorganic ions and saccharides and other organic materials in true solution, colloiddally dispersed macro-molecules of protein and polysaccharide, to spores of yeasts and moulds, and the largest particles, pollen grains.

Since the sugars are by far the most important constituents, the gross physical attributes of honey are largely determined by the kinds and concentrations of the carbohydrates. That these properties are expressed in ranges rather than by constants, reflects the variability in honey composition (largely in solids content) that was so evident in Chapter 5. Other properties, much less studied, are ordinarily reported as constants, though they probably would be found to vary over a range if enough samples were examined.

Though honey is superficially a syrup and an average of 84% of its solids consists of glucose (dextrose) and fructose (laevulose), its properties (viscosity, refractive index, density) differ somewhat from those of an invert-sugar solution of the same water content. These properties vary in a regular manner with the moisture content (or solids content) of honey, but some uncertainty as to actual values is caused by a lack of accuracy in methods for determining water content and by the possible effects of differences in ratios of the various sugars and in amounts of the more important minor components. Even so, each of these properties has

been used as a means of measuring the moisture content of honey—a value of great importance to the honey producer, packer, and merchant, since it bears a direct relation to the likelihood of undesired fermentation.

6.11 Moisture determination

Because a knowledge of procedures for direct determination of moisture content of honey is important in comparing the results of various investigators on the physical properties, a brief review follows.

These procedures may be considered in three categories: evaporation with measurement of weight loss, or with measurement of volume of water removed, and chemical determination. The first is most used; because of the sensitivity of honey sugars to heat, drying at a reduced temperature under reduced pressure is required. Generally an inert drying aid is added to increase bulk and porosity of the mass. Water may be added to the weighed sample to facilitate handling. The high hygroscopicity of dry honey requires the greatest care in manipulation.

As long ago as 1903 (Shutt & Charron, 1903), it was recognized that even in a vacuum at 70°C (158°F), fructose decomposition prevented the attainment of a constant weight; a temperature of 60–70°C (140–158°F) was recommended. Bryan (1908), however, questioned whether 70°C was sufficiently high to remove all water, but his reasons were based on a misconception; Fabris (1911) reported that 100° drying *in vacuo* gave results 0.3–0.5% higher than three other procedures, all of which gave agreeing values: drying at 60°C; a distillation method; drying in a dry air stream. Auerbach & Borries (1924) developed a method in which a 1 ml of a 50% solution is mixed with broken clay plate in a drying boat and dried at 60° in a current of dry air. Röttinger (1926) deposited a centigram sample on a roll of dry filter paper and heated at 100° *in vacuo*. Other procedures for increasing the surface area and preventing surface hardening during drying have been proposed, without bettering drying on sand below 70°C *in vacuo* (Marvin & Wilson, 1931, Rice & Boleracki, 1933, Schuette, 1935, Terrier, 1953, Kottász, 1958b). The Association of Official Analytical Chemists (Horwitz, 1965) uses a 1-g sample, mixes with sand, and dries at less than 70°C at a pressure not over 50 mm Hg until the weight is constant within 2 mg (which corresponds to about 0.2% water). Fulmer *et al.* (1934) proposed that the sample weight be increased to 5 g, claiming greater accuracy, but their data do not support this.

Distillation with turpentine, with measurement of recovered water, was one of the procedures tested by Fabris (1911) for honey moisture determination; for three samples results agreed with those of vacuum drying at 60°C. Abramson (1955) found that the Karl Fischer chemical titration for water gave values 0.29% moisture higher than vacuum drying at 70°C, with lower experimental error (0.14 against 0.33). Hadorn

(1956) confirmed that vacuum drying at 100°C (212°F) was unsatisfactory, as was Terrier's procedure. Further study of this application of the Karl Fischer procedure might be useful.

The direct drying procedure in any of its modifications is at best slow and cumbersome. Indirect methods have been studied, including refractometry at 20 or 40°C (68 or 104°F), density by pycnometer, relative density by spindle, and viscosity. Wedmore (1955) has written an excellent critical review of moisture determination in honey. He correlated the results of various investigators and proposed equations for the instrumental methods. Unfortunately, before his death he had completed only Part 1 of a projected six-part study of the subject, but it included his general conclusions. Pícha (1965) compared 12 procedures for determining moisture, using 15 honey samples. There were 3 refractometric, 5 drying, and 3 relative density methods, and a wet oxidation procedure. No significant differences were found among the methods; drying methods were recommended if the time required is not a factor. Refractometric methods, which are simple but of lower sensitivity, were sufficiently accurate to be recommended for processing control.

6.2 REFRACTIVE INDEX

As noted above, the primary interest in this property of honey is to provide a rapid, accurate, and simple measure of its moisture content. Early workers (Utz, 1908*b*, Bryan, 1908) noted that the moisture values obtained when converting refractometric readings by means of sucrose tables were higher by 1-2% moisture than those from vacuum drying. This was interpreted (Bryan, 1908) to mean that the latter method might not remove all water. Not until Auerbach & Borries (1924) studied the procedure was the necessity of special calibration for honey recognized. They calibrated the refractometer at 40°C (104°F) against a vacuum-drying procedure, using 23 samples of which only 10 were, however, fresh floral honeys. Auerbach & Borries provide the following relationship between dry substance and refractive index at 40°:

$$\text{dry matter } (T) = 78 + 390.7 (n_{40} - 1.4768)$$

This may be solved for n_{40} , to give $n_{40} = 0.002559T + 1.2772$ where T must be 78 or more.

In spite of this work, Marvin & Wilson (1931, 1932), Schenk (1934), Marvin (1933), and Snyder (1933) used sucrose tables for refractometric determination of moisture in honey. However, Chataway (1932) provided the definitive study of the relationship, calibrating the refractometer at 25°C (77°F) with vacuum-oven determinations for 60 honey samples and providing temperature correction factors which have been

corroborated (Snyder, 1933). Her values agreed quite well with those of Auerbach & Borries when the latter were converted to 25°C. Fulmer *et al.* (1934) felt that since the data from Auerbach & Borries, and Chataway, and the vacuum drying methods, gave values lower by 1.7% moisture than those obtained from sugar tables, it was advisable to modify the vacuum drying method to give higher water values! The modification they used was an increase of the honey sample to 5 g. Their refractometer calibration equation was then:

$$\text{percentage moisture} = 400 (1.5380 - n_{20})$$

These values are about 1% moisture below those in the Schönrock table, and 0.7% moisture higher than Chataway's. After several papers (Marvin & Wilson, 1931, 1932, Marvin, 1933) in which honey refractometric values were converted to Brix (% sucrose), Marvin (1934) finally published a table relating water content and refractive index, without attribution, which agreed with the Chataway data to within 0.0001-0.0002 units. Experimental data were not published. Eckert & Allinger (1939), in their analytical study of California honeys, determined moisture by drying (A.O.A.C.) and also by refractometer. They stated that they used the methods and tables of Marvin; however, the papers they cited contained only the Schönrock sucrose conversion. Study of the Eckert & Allinger values for moisture determination by refractometer shows that they actually used either the Chataway table or the 1934 table of Marvin noted above, and certainly not a sucrose table. Their data, therefore, may not provide an independent confirmation of Chataway's results, as thought by Wedmore (1955). Torrent (1949) did confirm the Chataway table. Wedmore gives the following as the best relationship obtainable from the data of Chataway, Eckert & Allinger and Torrent:

$$\text{water content} = \frac{1.73190 - \log (n_{20} - 1)}{0.002243}$$

Table 6.2/1 shows the refractive index of honey at moisture contents from 13.0 to 22.0%, as calculated by Wedmore (1955) from this relationship. The Table includes corresponding values for 40°C (104°F), calculated from the Auerbach & Borries (1924) equation.

Several subsequent workers compared the water content determined by refractometer and by other procedures, direct and indirect. In general the deviation between water content by two instrumental methods (refractive index, density, viscosity) was considerably less than between the drying procedure and any other, indicating the relative imprecision of the drying procedure (Abramson, 1953, Hadorn, 1956). In some cases it is possible to infer n_{20} values from published equivalent values (Brix), convert them to moisture values by the Chataway table, and compare

Table 6.2/1
Refractive index of honeys of different water contents¹

| <i>Water content (%)</i> | <i>Refractive index (20°C)²</i> | <i>Refractive index (60°F)³</i> | <i>Refractive index (40°C)</i> | <i>Water content (%)</i> | <i>Refractive index (20°C)</i> | <i>Refractive index (60°F)</i> | <i>Refractive index (40°C)</i> |
|--------------------------|--|--|--------------------------------|--------------------------|--------------------------------|--------------------------------|--------------------------------|
| 13.0 | 1.5044 | 1.5053 | 1.4998 | 18.0 | 1.4915 | 1.4925 | 1.4870 |
| 13.2 | 1.5038 | 1.5048 | 1.4993 | 18.2 | 1.4910 | 1.4920 | 1.4865 |
| 13.4 | 1.5033 | 1.5043 | 1.4988 | 18.4 | 1.4905 | 1.4915 | 1.4860 |
| 13.6 | 1.5028 | 1.5038 | 1.4983 | 18.6 | 1.4900 | 1.4910 | 1.4855 |
| 13.8 | 1.5023 | 1.5033 | 1.4978 | 18.8 | 1.4895 | 1.4905 | 1.4850 |
| 14.0 | 1.5018 | 1.5027 | 1.4973 | 19.0 | 1.4890 | 1.4900 | 1.4845 |
| 14.2 | 1.5012 | 1.5022 | 1.4968 | 19.2 | 1.4885 | 1.4895 | 1.4840 |
| 14.4 | 1.5007 | 1.5017 | 1.4962 | 19.4 | 1.4880 | 1.4890 | 1.4835 |
| 14.6 | 1.5002 | 1.5012 | 1.4957 | 19.6 | 1.4875 | 1.4885 | 1.4829 |
| 14.8 | 1.4997 | 1.5007 | 1.4952 | 19.8 | 1.4870 | 1.4880 | 1.4824 |
| 15.0 | 1.4992 | 1.5002 | 1.4947 | 20.0 | 1.4865 | 1.4875 | 1.4819 |
| 15.2 | 1.4987 | 1.4997 | 1.4942 | 20.2 | 1.4860 | 1.4870 | 1.4814 |
| 15.4 | 1.4982 | 1.4992 | 1.4937 | 20.4 | 1.4855 | 1.4865 | 1.4809 |
| 15.6 | 1.4976 | 1.4986 | 1.4932 | 20.6 | 1.4850 | 1.4860 | 1.4804 |
| 15.8 | 1.4971 | 1.4981 | 1.4927 | 20.8 | 1.4845 | 1.4855 | 1.4799 |
| 16.0 | 1.4966 | 1.4976 | 1.4922 | 21.0 | 1.4840 | 1.4850 | 1.4794 |
| 16.2 | 1.4961 | 1.4971 | 1.4916 | 21.2 | 1.4835 | 1.4845 | 1.4788 |
| 16.4 | 1.4956 | 1.4966 | 1.4911 | 21.4 | 1.4830 | 1.4840 | 1.4783 |
| 16.6 | 1.4951 | 1.4961 | 1.4906 | 21.6 | 1.4825 | 1.4835 | 1.4778 |
| 16.8 | 1.4946 | 1.4956 | 1.4901 | 21.8 | 1.4820 | 1.4830 | 1.4773 |
| 17.0 | 1.4940 | 1.4951 | 1.4896 | 22.0 | 1.4815 | 1.4825 | 1.4768 |
| 17.2 | 1.4935 | 1.4946 | 1.4891 | | | | |
| 17.4 | 1.4930 | 1.4940 | 1.4886 | | | | |
| 17.6 | 1.4925 | 1.4935 | 1.4881 | | | | |
| 17.8 | 1.4920 | 1.4930 | 1.4876 | | | | |

¹ The values for 20°C and 60°F are Wedmore's (Wedmore, 1955) calculations. The 40°C values are calculated from Auerbach & Borries' equation (Auerbach & Borries, 1924).

² If the R.I. is measured at a temperature above 20°C, add 0.00023 per °C above 20°C before using the Table.

³ If it is measured at a temperature above 60°F, add 0.00013 per °F above 60°F before using the Table.

these values with those reported in the publication by vacuum drying. Table 6.2/2 includes a comparison of the average deviations between the two procedures so calculated. Since refractometric values are relatively more precise, the high average deviations reflect the uncertainty in the determination of moisture by drying. The superiority of Chaatawy's data

is evident in the small value obtained for average deviation from her data. Zalewski (1962) compared pycnometry (20% solution) with refractive index at 40° and 20°C (68°F). For the last, the A.O.A.C. book is cited (which contains Chataway's table), but since Zalewski's values for solids at 20°C were on average 2.1% lower than those by the other two methods, it seems possible that the sucrose table therein was used. No specific citation was given. Abramson (1953) lists *S* (between duplicates) for 50 samples by 70° vacuum drying as 0.33; for refractive index with Chataway conversion (50 samples) as 0.06, and for Karl Fischer titration (148 samples) as 0.14.

Table 6.2/2
Average deviation between moisture content of honey
determined by direct drying and by refractometry

| <i>Investigator</i> | <i>No. samples</i> | <i>d</i> |
|-----------------------------|--------------------|-------------------|
| Bryan (1908) ¹ | 22 | 0.47 |
| Auerbach & Borries (1924) | 10 ² | 0.51 |
| Auerbach & Borries (1924) | 17 ³ | 0.47 |
| Chataway (1932) | 60 | 0.12 |
| Marvin & Wilson (1932) | 21 ⁴ | 0.76 |
| Fulmer <i>et al.</i> (1934) | 25 | 0.20 |
| Eckert & Allinger (1939) | 99 ⁵ | 0.28 |
| Torrent (1949) | 30 | 0.12 |
| Sacchi (1955) | 72 | 0.30 ⁶ |

¹ Dry substance converted to n_{28} by Geerling's table as given, converted to moisture by Chataway table, compared with vacuum-drying values.

² Fresh floral honeys only.

³ All floral honey samples.

⁴ First 21 samples in publication: n obtained from Schönrock table, converted to moisture by Chataway table, compared with vacuum-drying values.

⁵ Laevorotatory samples only.

⁶ After correction of errors in Sacchi's Table 2 (*see text*).

Sacchi (1955) has published a rather extensive study of moisture determination by refractometry for Umbrian (Italian) honey. Unfortunately, she chose the Fulmer *et al.* (1934) conversion table. She did find a better fit with her drying data if the equation of Fulmer *et al.* was modified by subtracting 0.32. Examination of her Table 2 shows 13 errors which, when corrected, revise the equation given by Sacchi to

$$\text{percentage water} = 400 (1.5380 - n_{20}) - 0.35.$$

This reduces the 0.7 difference between the higher values of the Fulmer

et al. (1934) conversion table and the Chataway values to half that amount.

It is impossible to separate the discussions of refractive index of honey and of its water content. The limiting factor in improving the accuracy of the Wedmore-derived relation is the independent direct method for moisture determination. Since the Karl Fischer method may have a lower error than oven drying (Abramson, 1953), and since a higher correlation coefficient was found (0.894) between Fischer and refractive index than between drying and refractometer (0.856), calibration of the refractive index method against moisture by Fischer titration might be considered. Abramson could not determine from his data which procedure should be the reference. From a practical viewpoint it is debatable whether further accuracy in moisture determination by refractometer would be significant, in view of the variations in honey composition. The calibrations given in Table 6.2/1 are at present more accurate than necessary for the hand refractometers that are in considerable use by honey producers and packers. Pearce & Jegard (1949) have calibrated such a refractometer against A.O.A.C. drying, and report a standard error of $\pm 0.4\%$ for the calibration. A standard error of $\pm 0.5\%$ was found for drying, and of $\pm 0.4\%$ for the refractometer. Thus the hand refractometer is much more convenient than the A.O.A.C. vacuum oven method, but not appreciably more accurate.

6.3 DENSITY AND RELATIVE DENSITY

The density of a substance is its mass per unit volume. In some countries the density of honey is expressed in pounds per gallon (U.S. or Imperial). The relative density (specific gravity) is the ratio of the mass of a given volume of a substance (at a stated temperature) to the mass of the same volume of water (at a stated temperature). Since water has a density of 1.0000g per ml at 4°C (39°F), relative density of a substance at any temperature (referred to water at 4°) is equal to the density at that temperature. The relative density of a liquid is determined by direct weighing of a known volume; it may also be determined by use of a calibrated hydrometer floating partially immersed in the liquid, or in other ways. There are numerous arbitrary calibrations of hydrometers for various purposes; some of those encountered in sugar analyses are Brix, Balling, Twaddell, and Baumé. In general, the use of hydrometers is potentially much easier and less expensive than pycnometry, but the nature of honey introduces such difficulty and uncertainty to the former that the two procedures are comparable.

6.31 Direct weighing methods (pycnometry)

Tables relating relative density to dry substance of sucrose solutions have

long been available, and have been much used in honey analysis. Fiehe & Stegmüller (1912), in comparing vacuum drying with density determination by pycnometer, noted differences in dry matter up to 1.5% with solutions of apparently equal density. They gave the relation $T = (d_4^{15} - 0.99913)/0.000771$ relating dry matter (T) with density (d). Auerbach & Borries (1924) determined d_4^{20} for 20% (w/v) honey solutions, using a 50-ml pycnometer, and also dry matter by direct drying using the same samples. For ten fresh floral honeys, the following relationships was obtained by the method of least squares:

$$T = (d_4^{20} - 0.99823)/0.00076763.$$

This was simplified to

$$T = 1302.7 (d_4^{20} - 0.99823),$$

the density value being that of a solution of 20.000 g honey in 100 ml water. In comparing values for water content calculated from this relation with those found by direct drying, for 17 samples, the average deviation obtained was 0.42% water. For comparison, a similar value for their refractometric procedure (drying vs. n) was 0.47% water.

Snyder (1933) compared density (in pounds per gallon) for 18 honey samples as determined: (a) by direct weighing of $\frac{1}{4}$ or $\frac{1}{2}$ pint; (b) by a pycnometer, using undiluted honey and converting the resultant d_{20} to weight per gallon from a sucrose table; (c) by refractometer converted to Brix and thence to weight per gallon by sucrose tables. The average values for the 18 samples by these procedures were 11.867, 11.867, and 11.859 lb/gal respectively. The average difference between (a) and (b) was 0.011; (b) and (c) 0.009; (a) and (c) 0.012. These differences are equivalent to 0.19, 0.16, and 0.21% water in the sucrose tables used. No relationship between moisture content of the honeys and density was determined or reported in this study.

Marvin (1933) described three procedures for determining the density of honey; one was the weighing of a standard pint or gill measure; another was the conversion of refractive index by sucrose tables to weight per gallon, both as described by Snyder (1933). Average values for 37 floral honeys were 11.838 and 11.845 lb/gal, respectively; the average difference was 0.015, equivalent to 0.26% moisture. Again, no independent determination of moisture content was made. This small difference is in contrast with the difference in moisture content between the sugar and honey calibrations of the refractometer in terms of solids (or water) content. Apparently, the refractive indices of honey and of a sucrose solution of equivalent density differ only slightly, the average difference being about 0.0006 in refractive index. By contrast, sucrose

solutions and honeys of equivalent moisture differ by about 0.0040 in refractive index, or about 1.6% moisture. When Marvin (1934) published a revised table relating refractive index, weight per gallon, and water content, the refractive index and weight per gallon relationship was not changed, though the water values in the revised table correspond to the Chataway equivalents.

Hadorn (1956) found an average difference between the Auerbach & Borries refractive index calculation and pycnometric determination of dry matter of 0.17% solids. The averages for the ten honeys were only 0.01% apart.

6.32 Hydrometry

Use of hydrometers for relative density determination in honey came many years after the development of these instruments for technical and research measurements in the sugar industry. Pique (1914) described a hydrometer for honey musts which had three graduations: relative density, weight of honey per hectolitre, and percentage of alcohol which should result from proper fermentation. Some use of hydrometers in honey processing was noted by Chataway (1932). In considering the use of the hydrometer for undiluted honey she noted that two such instruments were then in use in Canada, and examined both. One, designed for small honey samples, showed very poor reproducibility (over 2% moisture); the other (larger) was somewhat better. Later (Chataway, 1933) she designed a large, sensitive Baumé hydrometer for honey, and tested 38 honey samples whose moisture content was also determined by refractive index. In this work, earlier erratic results were eliminated by placing a layer of water on the honey surface after the hydrometer was in place. Readings were made at about 120°F and corrected to 68°F (20°C); they were also corrected for the presence of the water layer. Average moisture content for the 38 samples by refractometer was 17.42%, and by a calibration curve constructed from the hydrometer values, 17.43%. The average deviation between values by the two methods was 0.15% moisture.

Marvin (1933) described the use of a hydrometer for determining the weight per gallon of honey. This density measure was used because recently issued U.S. Department of Agriculture grades had specified a minimum density of 11.75 lb/gal at 68°F. Two procedures were described: use of a Brix hydrometer in warm full-density honey, and the Brix dilution method using a Brix hydrometer in a 1:1 dilution, then doubling the reading. Conversion to weight per gallon from Brix was made from standard sugar tables. Results from this latter method were compared with those from direct weighing and averaged (for 37 honeys) 11.915 lb/gal against 11.838 by weighing. The difference is equivalent to 1.35%

moisture. This value is close to the -1.3 correction which must be applied to Brix values of molasses when determined by the double dilution procedure, and is needed in that case to correct for the excess volume contraction of molasses over sucrose when diluted (Browne & Zerban, 1941, page 29). Marvin noted the higher values but ascribed no cause. Some of the physical difficulties of hydrometry in a heavy viscous liquid such as honey may be overcome by enclosing the sample in the instrument and suspending it in water. White (1967*b*) has made a preliminary evaluation of this type of hydrometer, the Eichhorn type, for moisture determination in honey. Sources of possible error were noted, and he concluded that the accuracy of his model was at least as good as that of the hand refractometer, perhaps better.

Wedmore (1955), while admiring Chataway's work on refractive index of honeys, felt that her work on relative density of honey 'though not yet superseded, is not in the same class'. He discussed two calibration charts (percentage of water vs. degrees Baumé) of Chataway: that in the original 1933 publication and one published later (Chataway, 1935). When converted to the same temperature basis they differ somewhat, particularly in the lower moisture ranges. Wedmore thought that this resulted from (a) using too few samples with a low moisture content (less than 15.5%), and (b) the straight-line relationship used for the later conversion table; in the 1933 paper a curve was shown to be necessary, and this is also true for other sugar solutions.

In Wedmore's Table 6, column 6 is entitled 'Author's new determination' and lists relative density values at $20^{\circ}/20^{\circ}$. Careful reading of the paper leads one to believe that this refers not to independent experimental work but to his fitting of a new line to the original Chataway data which he obtained from her Figure 2, from which Wedmore 'reproduced the original experimental results by the use of a reading microscope' (Wedmore, 1955). The relative density values in Wedmore's Table 6, column 6, differ from the 1935 Chataway table, and Wedmore noted that the relative density figures in the Chataway 1935 table suffered not only from the use of the linear relationship, 'but also from some error made during conversion to S.G.; it seems impossible now to trace this to its source, by its magnitude or otherwise . . . her published S.G. figures tend to give too low a water content, the difference in S.G. representing a difference in water content of about 0.2%'. The source of this difference now appears clear. In a letter written in 1937 to a U.S. Department of Agriculture official which has recently come to hand, Dr. Chataway commented on a Baumé-Brix conversion table in a 1933 Department honey-grading circular, pointing out that it did not agree with her table because two different Baumé scales were involved. The U.S. scale was the U.S. Bureau of Standards Bates and Bearce modifica-

tion (Browne & Zerban, 1941, page 81) established in 1918 and relating Baumé to relative density at 20°/20°C. Dr. Chataway used the older 'American Standard' Baumé which related to relative density at 60°/60°F. Since the differences between relative density values 20°/20° calculated from Baumé are about 0.0012-0.0016 in relative density in the proper direction, it is evident that Wedmore assumed that Chataway used the modern Baumé (20°/20°) when in fact she used 60°/60°, so her lower values resulted from her proper correction of the relative density 60°/60° values obtained from the Baumé equation* to relative density 20°/20° values, which Wedmore did not do. An example will perhaps clarify this explanation. Wedmore notes that Chataway's values (in Baumé degrees) in the middle of the range are practically identical with his newly calculated figures. Her Table 2 (Chataway, 1933) gives for 17.4% moisture a Baumé value at 68°F of 42.89. Converting by her value of 0.024 per degree F, we obtain 43.08 Bé at 60°F (her 1935 table gives 43.09). Since the Baumé scale Chataway used was the older American scale, the relative density at 20°/20° is obtained as follows:

$$\begin{aligned} \text{R.D. } 60^{\circ}/60^{\circ}\text{F} &= 145 / (145 - 43.08) \\ &= 1.42268 \end{aligned}$$

Using Wedmore's conversion factors to convert 60°/60°F to 20°/20°C, we have R.D. 20°/20°C = (1.42268 × 1.00081) - 0.0027 = 1.42113, which rounds to 1.4211. The corresponding value in the 1935 Chataway table is 1.4212. If we assume (as apparently Wedmore did) that the 'new' Baumé scale was used, we get

$$\begin{aligned} \text{R.D. } 20^{\circ}/20^{\circ} &= 145 - (145 - 43.08) \\ &= 1.42268 \end{aligned}$$

which rounds to 1.4227. The value given by Wedmore in his Table 6, column 6, is 1.4226 for his 'new' determination.

We must therefore conclude that Wedmore's new curve was obtained from Chataway's experimental Baumé values, but erroneously converted to relative density. We cannot then accept his Table 5, 'Proposed figures for the specific gravity [relative density] of honeys of different water contents' because the values he labels relative density 20°/20°C are in fact relative density 60°/60°F and must be converted (as indicated above) to obtain the 20°/20°C table.

Table 6.32/1 shows the Wedmore revision of Chataway's data, converted correctly to relative density. Departure from the 1935 Chataway table is primarily at the lower-moisture end, and the two tables are coincident between 17.2 and 19.2% moisture.

* Degrees Baumé = 145 - 145 / (R.D. 60°/60°); Bur. Stds. Bé = 145 - 145 / (R.D. 20°/20°).

The specification 'modulus 1.45' used by Chataway (Chataway, 1935) is not sufficient to identify the Baumé scale she used. It is true that other scales use different moduli, but the Bates-Bearce scale differed

Table 6.32/1
True specific gravity of honeys of different water contents*

| Water content % | Specific gravity 20/20°C | Specific gravity 60/60°F | Water content % | Specific gravity 20/20°C | Specific gravity 60/60°F |
|-----------------|--------------------------|--------------------------|-----------------|--------------------------|--------------------------|
| 13.0 | 1.4457 | 1.4472 | 17.0 | 1.4237 | 1.4252 |
| 13.2 | 1.4446 | 1.4461 | 17.2 | 1.4224 | 1.4239 |
| 13.4 | 1.4435 | 1.4450 | 17.4 | 1.4211 | 1.4226 |
| 13.6 | 1.4425 | 1.4440 | 17.6 | 1.4198 | 1.4213 |
| 13.8 | 1.4414 | 1.4429 | 17.8 | 1.4185 | 1.4200 |
| 14.0 | 1.4404 | 1.4419 | 18.0 | 1.4171 | 1.4187 |
| 14.2 | 1.4393 | 1.4408 | 18.2 | 1.4157 | 1.4173 |
| 14.4 | 1.4382 | 1.4397 | 18.4 | 1.4143 | 1.4159 |
| 14.6 | 1.4372 | 1.4387 | 18.6 | 1.4129 | 1.4145 |
| 14.8 | 1.4361 | 1.4376 | 18.8 | 1.4115 | 1.4131 |
| 15.0 | 1.4350 | 1.4365 | 19.0 | 1.4101 | 1.4117 |
| 15.2 | 1.4339 | 1.4354 | 19.2 | 1.4087 | 1.4103 |
| 15.4 | 1.4328 | 1.4343 | 19.4 | 1.4072 | 1.4088 |
| 15.6 | 1.4317 | 1.4332 | 19.6 | 1.4057 | 1.4073 |
| 15.8 | 1.4306 | 1.4321 | 19.8 | 1.4042 | 1.4058 |
| 16.0 | 1.4295 | 1.4310 | 20.0 | 1.4027 | 1.4043 |
| 16.2 | 1.4284 | 1.4299 | 20.2 | 1.4012 | 1.4028 |
| 16.4 | 1.4272 | 1.4287 | 20.4 | 1.3996 | 1.4012 |
| 16.6 | 1.4260 | 1.4275 | 20.6 | 1.3981 | 1.3997 |
| 16.8 | 1.4249 | 1.4264 | 20.8 | 1.3966 | 1.3982 |
| | | | 21.0 | 1.3950 | 1.3966 |

* Wedmore's (Wedmore, 1955) revision of Chataway's (Chataway, 1933) data as corrected (see text). By definition, values for S. G. 20°/20° calculated from Baumé are 'true' specific gravity, i.e. they correspond to weight *in vacuo*. To obtain 'apparent' specific gravity, i.e. corresponding to weight in air with brass weights, the correction to be added to the true value varies from 0.00047 at 21% moisture to 0.00055 at 13% moisture. An average correction of +0.0005 is satisfactory. The term 'relative density' is now preferred to 'specific gravity'.

from the older American standard only in the use of R.D. 20°/20°C rather than R.D. 60°/60°F, and it uses the same modulus. The newer scale appears to be in general use in the U.S.A. (Browne & Zerban, 1941, page 82; Bates *et al.*, 1942, page 249). Chataway anticipated confusion, for in the letter noted above she remarked that the Bates-Bearce scale is still recognized, apparently, as it appears in the fourth, 1936, edition of the *American Official Agricultural Handbook** . . . but it can hardly be considered correct. In effect it establishes a second American Baumé scale with no convenient title to distinguish it from the one more generally recognized.

The relatively large range of honey densities requires that particular care be taken to ensure thorough mixing when honeys are blended. Layering of different honeys in a tank can be quite pronounced; in fact, Fix & Palmer-Jones (1949) state that the reason why the top layer of honey in settling tanks is the most dilute is density difference rather than absorption of moisture from the air. Heating with mixing is recommended to avoid such layering.

6.33 Other methods

A very approximate measurement of the 'consistency' of honey is described by Hansson (1966). A cone is supported point down, touching the honey surface, and is then released. Consistency (on a scale 1 to 5) is evaluated from the rate of sinking and the final depth. A field test for the maximum water content of honey that is inexpensive, easy, and rapid, is described by Aganin (1965). To determine whether honey contains more or less than 22% water by volume, a drop is added to a water solution of calcium perchlorate having the same relative density; if it rises to the surface it is less dense than the solution, and hence is presumed to contain more than 22% water.

6.4 VISCOSITY AND THIXOTROPY

This subject has been reviewed by Pryce-Jones (1953) in his article 'The rheology of honey' in Scott-Blair's book. No significant fundamental contribution to the field has come to hand since that time, so this discussion will be restricted to a brief review.

6.41 Viscosity for determining moisture

Von Fellenberg (1911) attempted to use viscosity measurement to

* This table appears in the 1965 Tenth edition. It gives 'true specific gravity', corresponding to weights *in vacuo*, calculated directly from the formula. Table 3 in Browne & Zerban (1941) also gives the Bates-Bearce scale, but is calculated to give 'apparent relative density' at 20°/20°C, which corresponds to weighing in air.

detect the addition of glucose syrup to honey. Considerable variation in the viscosity of different honeys reduced the value of the method. In the study of the effect of moisture content on various physical attributes of honey already discussed, Chataway (1932) included viscosity measurement. Using a falling-ball viscometer, she reported a nearly straight-line relationship between *log* viscosity and *log* moisture content. Using this curve, moisture contents for the 60 honeys were calculated and compared with those obtained by the A.O.A.C. vacuum drying procedure. The average difference for all samples was 0.20% moisture; elimination of 5 buckwheat samples which did not fit the curve reduces this to 0.14% moisture. Chataway noted that a difference of 0.1% in moisture gives viscosity differences of 4-6%. The viscosity of honey is highly temperature-sensitive; Chataway constructed a correction chart by which the times of fall at any temperature between 15.0 and 30.0°C (59-86°F) to 0.1°C could be corrected to 25.0° before conversion to moisture values.

Oppen & Schuette (1939) found a very low correlation between refractive index and moisture content of honey by the A.O.A.C. drying method (no data are given), so they investigated the use of viscosity for determining moisture content. They criticized Chataway's apparatus as permitting errors up to 8% because of wall effects, due to the use of a too-narrow tube. Using an apparatus with a more favourable ratio of ball diameter to tube diameter, they determined viscosities of 30 samples at 40°C (104°F), and of 15 at four other temperatures. An equation relating viscosity, moisture content, and temperature was developed, and a graph was presented from which moisture content could be obtained from the time of fall of the ball in their apparatus (Figure 6.41/1). The time is determined at a known temperature between 30° and 50°C (86 and 122°F) for a steel ball of diameter 0.16 cm (0.06 or $\frac{1}{16}$ in) to fall 20 cm through the centre of a 25-mm standard-wall pyrex tube containing the honey, after gravity acceleration in the honey for 8 cm. This time-temperature point is located on the graph, and a line parallel to the nearest diagonal line intersects the *W* scale at the water content of the honey.

The average difference between moisture values found by Oppen & Schuette from the chart and from the A.O.A.C. method is 0.20%. Since they claimed their procedure to be more accurate than Chataway's, her lower average deviation may arise from a better technique for A.O.A.C. moisture determination.

6.42 Absolute values for viscosity

Neither Oppen & Schuette nor Chataway provided absolute values for viscosity. Lothrop (1939) did so in a study of the effect of composition of honey on viscosity. Even when adjusted to equal moisture content,

the viscosity (at 40°C, 104°F) varied from 3.10 poise for alfalfa honey (*Medicago sativa*) to 4.11 for sumac honey (*Rhus*). Only four honeys were within the range 3.10-3.14 poise. (Two honey samples, one from honeydew in Hawaii, and one from tarweed (*Hemizonia*) with an anomalous

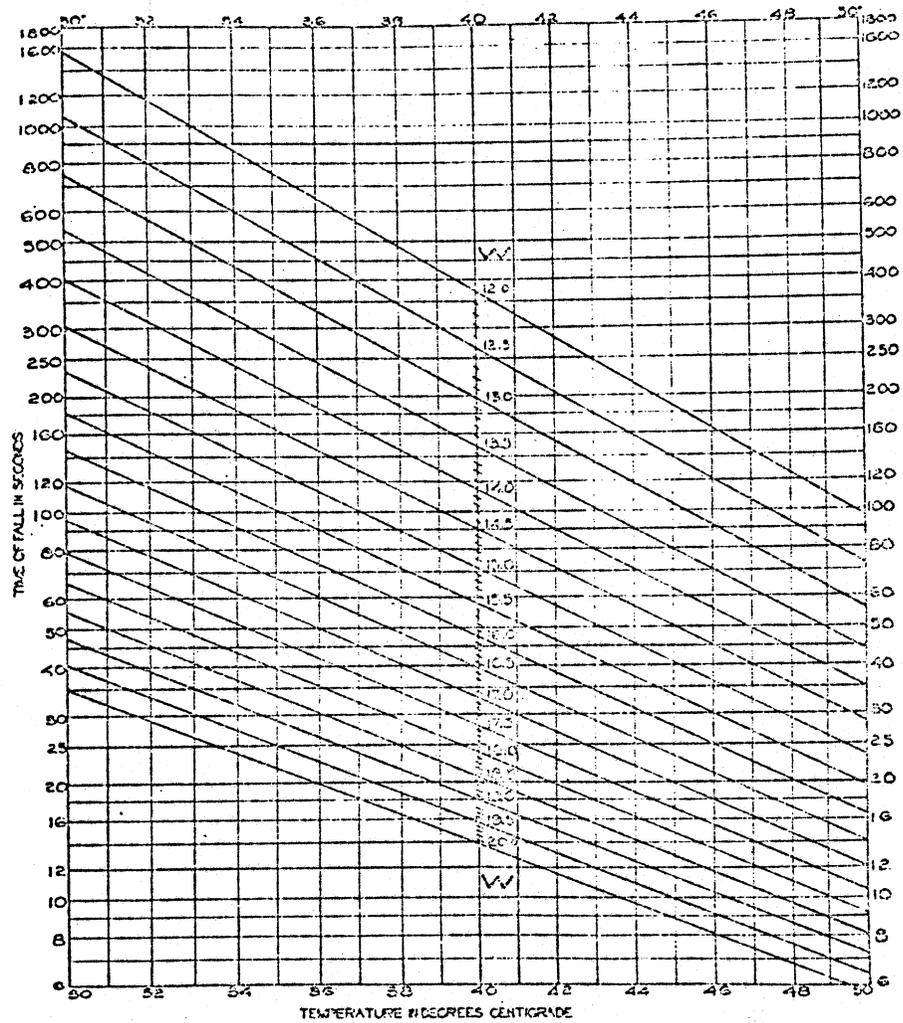


Figure 6.41/1 Relation between (a) time of fall of a ball through honey in the Oppen & Schuette (1939) viscosity apparatus at given temperatures and (b) moisture content (W) of honey (see text for details).

composition, are not included in this discussion.) Lothrop believed that viscosity variations in honey are due to non-sugar materials, particularly 'dextrins', and that colloidal materials also help to determine the viscosity.

The work of Munro (1943) appears to be the most extensive. Using a MacMichael viscometer, he determined viscosity for sweet clover honey (*Melilotus*) at 6 moisture contents, sage honey (*Eriogonum*) at 3, and white clover honey (*Trifolium repens*) at 9. He included several further samples, some with colloids removed. The viscosity of each was measured at a number of temperatures, about 3°C apart, over the range 5–80°C

Table 6.42/1
Viscosity of honey

| Type | Moisture content (%) | Temperature (°C) | Viscosity (poise) |
|--|----------------------|------------------|-------------------|
| Sweet clover ¹ (<i>Melilotus</i>) | 16.1 | 13.7 | 600.0 |
| | | 20.6 | 189.6 |
| | | 29.0 | 68.4 |
| | | 39.4 | 21.4 |
| | | 48.1 | 10.7 |
| | | 71.1 | 2.6 |
| Sage ¹ (<i>Eriogonum</i>) | 18.6 | 11.7 | 729.6 |
| | | 20.2 | 184.8 |
| | | 30.7 | 55.2 |
| | | 40.9 | 19.2 |
| | | 50.7 | 9.5 |
| White clover ² (<i>Trifolium repens</i>) | 13.7 | 25.0 | 420 |
| | | | 269 |
| | | | 138 |
| | | | 69.0 |
| | | | 48.1 |
| | | | 34.9 |
| | | | 20.4 |
| | | | 13.6 |
| Sage ² | 16.5 | 25 | 115 |
| Sweet clover ² | 16.5 | 25 | 87.5 |
| White clover ² | 16.5 | 25 | 94.0 |

¹ Data of Munro (1943)

² Interpolated from Munro's data

(41-176°F). Whereas Oppen & Schuette obtained straight lines for *log* viscosity plotted against $1/T$ over their range of 30-50°C (86-122°F), Munro's data over the much wider range show a slight curve, characteristic of a highly associated liquid. Table 6.42/1 gives typical viscosity values observed by Munro. To facilitate comparison, the Table includes a number of values obtained from the Munro data by graphical interpolation.

Munro (1943) noted that the viscosity of honey changes most rapidly as the temperature rises to room temperature, and stated that the rate of viscosity decrease drops markedly from room temperature to about 30°C, and thereafter shows relatively little change. These observations were based on his plotting of the data on a direct basis. The Pryce-Jones plot (Pryce-Jones, 1953) of Munro's values as *log* viscosity against $1/T$ shows that the rate of change is relatively constant. Munro stated that heating honey above about 30°C (except for low-moisture types) produces such slight viscosity decreases as to be without practical significance. He noted that 1% moisture is equivalent to about 3.5°C in its effect on viscosity. However, MacDonald (1963) has examined the effect of temperature on honey pumping rates and on flow through pipes of various sizes. Table 6.42/2 shows his data for the flow of honey at constant

Table 6.42/2
Relative flow of honey in pipes*

| Pipe diameter (inside) | Temperature | | |
|----------------------------|-------------|--------------|--------------|
| | 82°F (28°C) | 102°F (39°C) | 122°F (50°C) |
| $\frac{3}{4}$ in (19 mm) | 149 | 400 | 1 125 |
| 1 in (25 mm) | 367 | 973 | 2 353 |
| 1 $\frac{1}{4}$ in (31 mm) | 729 | 1 895 | 5 000 |
| 1 $\frac{1}{2}$ in (38 mm) | 1 263 | 2 609 | 6 792 |

* Rate of flow (in pounds per hour) through 4-in. (10-cm) length of pipe with 4-in. head. Data of MacDonald (1963).

pressure head of honey (4 in., 10 cm, to top of outflow) through a 4-in. length of horizontal pipe at three temperatures. The difference between flow rates at 102°F (39°C, well above Munro's 30°C) and 122°F (50°C) is quite significant; the relative increase is equal to that from 82°F (28°C) to 102°F (39°C), as expected from viscosity data. From the point of view

of maintaining quality of honey, however, it is better to increase capacity in honey pumping and handling by increasing pipe and pump size than by increasing temperatures excessively. However, contrary to Munro's view, temperatures over 30°C (86°F) can be significant in facilitating honey handling.

6.43 Non-Newtonian properties

In addition to the behaviour of honeys as Newtonian liquids, described above, certain non-Newtonian rheological phenomena have been reported. Thixotropy, an isothermal reversible gel-sol-gel transformation induced by shearing and subsequent rest, is quite pronounced in honey from heather (*Calluna vulgaris*) and a few other sources. Without agitation, this honey will not flow sufficiently for extraction in a centrifugal extractor. Pryce-Jones (1953) has extensively reviewed the rheology of heather honey. He notes that manuka (*Leptospermum scoparium*) honey of New Zealand is also markedly thixotropic. The property is ascribed for both honeys to their relatively high content of certain proteins; the heather honey protein can render clover honey thixotropic. Deodikar *et al.* (1957) report that karvi honey (*Carvia callosa*) from India is also markedly thixotropic.

Another non-Newtonian response is 'dilatancy'; this is increased viscosity with increased rate of shear. Pryce-Jones (1952) notes that several honeys—*Opuntia engelmanni* from Nigeria and several *Eucalyptus* species—possess this property to a rather high degree; he ascribes it to their content of the polysaccharide dextran of molecular weight in the 1 250 000 range. Also known as *Spinnbarkeit* or 'stringiness', it is easily noted by the formation of long 'strings' on honey when a rod is dipped into it and rapidly moved away.

6.44 Diffusivity

The apparent diffusivity of water in honey was measured by Fan & Tseng (1967), using a laser interferometric microdiffusion cell. It was highly dependent on concentration and was of the same order of magnitude as that of a glucose solution in water.

6.5 OPTICAL PROPERTIES

Relative little attention has been given to the various optical properties of honey, with the exception of optical rotation.

6.51 Optical rotation

Among many other materials of natural origin, honey has the property of rotating the polarization plane of polarized light. This is one further

property that depends largely on the sugars of honey—their types and relative proportions. Since each sugar has a specific and consistent effect, and the total optical rotation is dependent on concentration, analysts early used optical rotation under various specified conditions as a means of sugar analysis. It was quite precise and accurate in the analyses encountered in the sugar industry and, with the relatively simple view of the sugars of honey then current, the use of the method was extended for sugar analysis of honey. The limitations of the method (White, Ricciuti & Maher, 1952) are such that modern honey analysts have largely abandoned it. One generalization that appears to remain valid is that floral honeys are laevorotatory and honeydew (or adulterated) honeys are usually dextrorotatory. This is a consequence of the normal preponderance in floral honey of fructose, which has a negative specific rotation, $([\alpha]_D^{20} = -92.4^\circ)$ over glucose $([\alpha]_D^{20} = +52.7^\circ)$. Honeydew types are usually somewhat lower in fructose content and contain mellezitose $[\alpha]_D^{20} = +88.2^\circ$ or erlose $([\alpha]_D^{25} = +121.8^\circ)$ (White & Maher, 1953*b*) which, together with glucose, usually give a positive net optical rotation.

6.52 Mutarotation

Many sugars are capable of existing in solution in several physical forms, which may have different optical rotations. Usually, a sugar exists in one form in the crystal. On dissolving, an equilibrium is reached between the several forms; during the equilibration process the optical rotation of the solution changes. This is mutarotation (multirotation), and the extent is quite characteristic of specific sugars.

Honey, although completely liquid, will exhibit a slow change in optical rotation after being diluted. In Browne's (1908) analyses, 92 samples of laevorotatory honeys showed a change of -3.5° after standing for 20 hr. The change is not brought about by the difference in specific rotation of the sugars due to the concentration change; this would be in the opposite direction and largely due to fructose. A pronounced mutarotation would of course be expected when the honey being dissolved contains glucose crystals. Even when the honey is entirely liquid, the net change in optical rotation on solution is in the direction of glucose mutarotation, not that of fructose; furthermore, fructose mutarotation is about 12 times as rapid as that of glucose. It seems likely that glucose is involved in honey mutarotation. No studies of the cause or mechanism of honey mutarotation are at hand.

6.53 Colour of honey

Much of the literature on honey colour is simply descriptive, relating colour to floral source and processing of honey. As noted in Chapter 5, relatively little is known of the compounds responsible.

Colours of honey form a continuous range from very pale yellow through ambers to a dark reddish amber to nearly black. Greenish casts are fairly common. Colour ranges are generally characteristic for floral type. Brice *et al.* (1956) made a rather extensive physical examination of honey colour in establishing the current U.S. Department of Agriculture honey colour classes, recording spectrophotometric data for several characteristic honeys in all colour ranges, and calculating CIE colorimetric data. They concluded that the principal colorants of honey, maple syrup, caramel solutions and other sugar products are similar, basing this view on strong similarity in the plotted values of $\log A v.$ wavelength for the various products. Honey shows more minor departures from linearity than do other products.

Honey appears to be lighter in colour after granulation than when liquid. The crystal size affects the degree of lightening, the finest crystals imparting the lightest shade. Two explanations may be advanced for this: (a) the opacity of granulated honey greatly reduces the thickness of the honey layer actually being observed; and (b) increasing whiteness is imparted to a material by reducing its particle size. The increase in the proportion of surface-reflected light in the total may account for this type of lightening.

Colour of honey is important in its marketing. This is dealt with in Chapters 12 and 13. References to colour grading in various countries include systems used in Hungary (Kottász, 1958a), U.S.S.R. (Kottász, 1958a), Britain (British Standards Institution, 1952), France (Barbier & Valin, 1957), U.S.A. (United States Department of Agriculture, 1951), Canada (Canada Department of Agriculture, 1952, Townsend, 1969a), and Australia (1964).

It is well known that honey darkens in colour during storage. One of the most extensive studies of the effect of storage on honey colour is that of Milum (1948). He concluded that discoloration during storage is in part dependent upon the amount of previous discoloration, and that discoloration during processing tends to lessen the subsequent rate of discoloration. Table 6.53/1 shows a summary of Milum's data obtained by replotting his values and interpolating. These values are approximations and useful to indicate order of magnitude only. Great variation in darkening rate is found among different honeys, depending upon their composition (acidity, nitrogen and fructose contents). F. G. Smith (1967) examined the darkening effect of storage at several temperatures between 43° and 80°C upon several Australian honeys. The variability in response by different honeys was confirmed; one honey (from *Dryandra sessilis*) darkened twice as rapidly as any other. Smith noted a correlation between the time required at a given temperature to effect a 10-mm (Pfund) increase in colour and the time required to produce 3 mg

Table 6.53/1
Approximate rate of honey darkening in storage*

| <i>Temperature of storage</i> | | <i>Darkening in mm Pfund/month</i> | | |
|-------------------------------|------|---------------------------------------|-------------------------------------|---------------------------------------|
| °F | °C | <i>Original colour < 34 mm</i> | <i>Original colour 34-50 mm</i> | <i>Original colour > 50 mm</i> |
| 50 | 10.0 | 0.024 | 0.024 | 0.024 |
| 60 | 15.6 | 0.08 | 0.125 | 0.10 |
| 70 | 21.1 | 0.27 | 0.70 | 0.40 |
| 80 | 26.7 | 0.90 | 4.0 | 1.50 |
| 90 | 32.2 | 3.0 | 7.7 | 5.0 |
| 100 | 37.8 | 10.0 | 14.0 | 11.0 |

* Calculated from data of Milum (1948)

hydroxymethylfurfuraldehyde per 100 g honey at the same temperature (White, Kushnir & Subers, 1964).

Irradiation by ultraviolet excites fluorescence in honeys, the emitted colours differing among various honey types. The work of Orbán & Stitz (1928) appears to be the only study of the phenomenon.

6.6 THERMAL PROPERTIES

The physical properties of honey with regard to heat have received only minimal attention, though the chemical and biological effects of heat have been studied extensively. Presumably, the design of the minor amount of processing equipment originally intended for honey has largely been made by cut-and-try methods or by extrapolation from sugar data.

6.61 Specific heat

Helvey (1954) has determined several heat-related properties of honey. Using conventional methods, he reported that the specific heat of honey containing 17.4% moisture is 0.54 at 20°C (68°F), and the temperature coefficient 0.02 cal/°C.

MacNaughton, according to Townsend (1954), has also determined the specific heat of honey. He used a sample about seven times as large as Helvey's, and a temperature range of 29-48°C (85-119°F). He obtained somewhat higher results, shown in Table 6.61/1; they are believed to be accurate to ± 0.02 . Both investigators ascribed small variations to the effect of honey composition.

Table 6.61/1
Specific heat of honey*

| <i>Moisture content (%)</i> | <i>Specific heat</i> |
|-----------------------------|----------------------|
| 20.4 | 0.60 |
| 19.8 | 0.62 |
| 18.8 | 0.64 |
| 17.6 | 0.62 |
| 15.8 | 0.60 |
| 14.5 | 0.56 |
| coarsely granulated | 0.64 |
| finely granulated | 0.73 |

* Data of MacNaughton (Townsend, 1954)

6.62 Thermal conductivity

Helvey (1954) determined the thermal conductivity of honey solutions, over the range 0% to 90% water, at various temperatures; he presented the results in a three-dimensional figure. The data in Table 6.62/1 were obtained from Helvey's Figure 5 by tracing upon graph paper. He also reported that finely crystallized honey at 20°C (68°F) has a thermal conductivity of 129×10^{-5} cal/cm sec°C. Detroy (1966) determined the surface conductance, or film coefficient, for honey within the processing temperature range, using a concentric-tube counter-flow heat-exchanger. Values were obtained at honey flow rates between 700 and 900 lb/hr (317-442 kg/hr) and speeds from 0.17 to 0.24 ft/sec (5.2-7.3 cm/sec). Values ranged from 34.1-40.1 BTU/sq ft/hr/°F (preheater water circuit) to 57.7-77.0 BTU/sq ft/hr/°F (flash-heater water circuit).

6.63 Freezing point of solutions

Full-density liquid honey becomes increasingly hard as the temperature is reduced, but water does not appear to crystallize from it.

Stitz & Szigvárt (1931a) studied the freezing point of honey. Because of its physical nature they were unable to obtain values for honey solutions more concentrated than 68%, for which they found a freezing-point depression of 12.01°C (21.6°F). Agreement was excellent between the freezing points found for 15% honey solutions and values calculated from the concentrations of glucose, fructose, and sucrose: -1.44 and -1.438°C (29.41°F), -1.49 and -1.49°C (29.32°F).

For ten honeys, the freezing point of 15% solutions ranged from -1.42 to -1.53°C (29.44 to 29.25°F).

Table 6.62/x
Thermal conductivity of honey*

| <i>Moisture content (%)</i> | <i>Temperature (°C)</i> | <i>Thermal conductivity (cal/cm sec °C)</i> |
|-----------------------------|-------------------------|---|
| 21 | 2 | 118×10^{-5} |
| | 21 | 125 |
| | 49 | 132 |
| | 71 | 138 |
| 19 | 2 | 120 |
| | 21 | 126 |
| | 49 | 134 |
| | 71 | 140 |
| 17 | 2 | 121 |
| | 21 | 128 |
| | 49 | 136 |
| | 71 | 142 |
| 15 | 2 | 123 |
| | 21 | 129 |
| | 49 | 137 |
| | 71 | 143 |

* Interpolated from graph of Helvey (1954)

6.64 Calorific value

Calculations by the Consumer and Food Economics Research Division of the U.S. Department of Agriculture (Watt & Merrill, 1963), using the Atwater system as reviewed by the F.A.O./U.N., give 1380 Cal/lb (304 Cal/100 g) for the energy value of an average sample of honey.

6.7 CRYSTALLIZATION

Glucose monohydrate spontaneously crystallizes from many honeys, which are supersaturated solutions under ordinary storage conditions. Whether they are also supersaturated under hive conditions at higher temperatures is not known, partly because the carbohydrate composition of honey is more complex than the model systems examined to date.

We are here concerned with general aspects of honey crystallization. Discussion of controlled granulation of honey, and of delaying granulation in liquid honey, are to be found in Chapters 9 and 10.

6.71 Model systems and honey composition

A possible route to understanding honey granulation lies in a study of phase relationships in model systems of sugars. An early attempt was that of Jackson & Silsbee (1924), who studied several systems at 30°, and discussed saturation relations in honey in the light of their data on the glucose-fructose-water system. They found that glucose solubility decreased with increasing laevulose concentration. With glucose hydrate as the solid phase, they recorded solubility at 54.64% without fructose, dropping to 32.55% at 39.4% laevulose.

Basing their calculations on the honey analyses of Browne (1908), Jackson & Silsbee (1924) concluded that all honey is supersaturated at 23°C (73°F); calculated supersaturation coefficients were 2.86 for alfalfa (*Medicago*) honey, and 1.66 for tupelo (*Nysssa*) honey which is known never to granulate. This apparent conflict was ascribed to the 'sluggishness with which dextrose crystallizes from solutions of high laevulose content'. The discrepancy is not due simply to the too-high dextrose values generally obtained by the older methods of analyses, since calculations based on recent analyses also imply supersaturation. Lothrop (1943), in an unpublished thesis, pointed out that Jackson & Silsbee's measurements did not extend to the laevulose concentrations often encountered in honey. Because of the past unavailability of this work, it is discussed here in some detail. Lothrop did not accept the explanation given by Jackson & Silsbee, noting that some honeys do not granulate even after many years, and even after seeding with dextrose hydrate. Lothrop studied the solubility of dextrose in laevulose solutions at concentrations extending to those found in honey. He found an abrupt (so sharp as to be transitional) increase in dextrose solubility at a laevulose concentration of about 150 g in 100 g water. In the area of lower solubility (85-90 g dextrose per 100 g water) the solid phase was dextrose monohydrate; beyond the higher solubility region (125-128 g per 100 g water) the solid phase was anhydrous dextrose. The equilibrium conditions were approached from both the undersaturated and oversaturated sides. Solubility curves were determined at 20°, 25°, 30°, and 52°C (68°, 77°, 81°, and 128°F) with both forms of dextrose, singly, as the initial solid phase. Solubility of sucrose (which does not hydrate) did not show the abrupt increase with increasing laevulose concentration. The curve for dextrose at 52°C (above the 50°C transition point for dextrose to dextrose hydrate) also did not show the break, and resembled the sucrose curve. Identification of the solid phase was by microscopic examination, the hydrate being stated to appear in hexagonal plate-like monoclinic crystals, with the anhydrous form as rhombic needle-like forms.

Lothrop believed that the change in solubility of dextrose was not

related to the α - β -equilibrium, but rather to the degree of hydration of the dextrose in solution; anhydrous dextrose is known to be more soluble than the hydrate. He lists six arguments for this hypothesis, based on his data. Later Kelly (1954) published the complete diagram for the system at 30°C (81°F)—without knowledge of Lothrop's work. Kelly also noted an area in which anhydrous dextrose is in the solid phase, with an invariant point at which both forms of dextrose are in equilibrium. He proposed that the presence of fructose had the effect of reducing the transition temperature of the monohydrate from above 50°C (122°F) to something less than 30°C (86°F) for solutions saturated with fructose. He noted that published analyses of honey relate to the area in which anhydrous glucose is the solid phase at 30°C. Since dextrose does not normally granulate from honey until the temperature is appreciably below 30°C, the crystallization seems to occur below the transition temperature so that it would appear as the monohydrate.

However, Villumstad (1952) has described the simultaneous occurrence in granulated honey of both needles and plates of dextrose, though he does not speculate on the reasons for the different forms. He reported that examination of the chemical and physical composition of the different crystals was in progress. Dean (1974) has described a new metastable β -glucose hydrate which may explain some of these anomalies.

6.72 Prediction of tendency to granulate

In view of the variations in honey composition, a means of predicting the granulation behaviour of a particular batch of honey would be of considerable practical interest. Rational selection of honey for liquid-honey packs, and blending for packs of finely crystallized honey of desired hardness characteristics, could be done on a routine basis.

All attempts to accomplish this have been empirical, using various proposed indices to fit the granulation behaviour observed after storage. Unfortunately, data at hand from model systems are not helpful; Jackson & Silsbee's diagrams do not extend to areas of interest; Lothrop's cover a wider range but are also not complete; Kelly's data are valid only at 30°C, at which no honeys granulate. White, Riethof, Subers & Kushnir (1962) have discussed the relation of the granulating tendency of honey to its composition, based on their observations and analyses of nearly 500 honey samples. Using statistical procedures, they showed highly significant correlations between granulating tendency and several previously proposed indices, the unadjusted dextrose/water ratio of Austin (1958) giving the highest value. The laevulose/dextrose ratio, much used in the past, was the lowest-ranking index. When applied to individual samples rather than to group averages, a slightly higher score was found for

Jackson & Silsbee's $(D-W) \div L$ value. The difference was quite small, and since Austin's factor does not require determination of laevulose, it is preferred. The average D/W ratios for 477 honeys placed in ten granulation classes (White *et al.*, 1962) are shown in Table 6.72/1.

Table 6.72/1
Average dextrose-water ratios for honeys
classified by granulation characteristics¹

| <i>Extent of granulation</i> ² | <i>No. samples</i> | <i>D/W</i> |
|---|--------------------|------------|
| none | 96 | 1.58 |
| few scattered crystals | 114 | 1.76 |
| 1.5-3 mm layer of crystals | 67 | 1.79 |
| 6-12 mm layer of crystals | 68 | 1.83 |
| few clumps of crystals | 19 | 1.86 |
| $\frac{1}{4}$ of depth granulated | 32 | 1.99 |
| $\frac{1}{2}$ of depth granulated | 19 | 1.98 |
| $\frac{3}{4}$ of depth granulated | 16 | 2.06 |
| complete soft granulation | 18 | 2.16 |
| complete hard granulation | 28 | 2.24 |

¹ Data of White, Riethof, Subers & Kushnir (1962)

² Granulation observed in heated honey after 6 months undisturbed storage at 23-28°C; honey in $\frac{1}{2}$ lb or 1 lb jars (0.23, 0.45 kg).

Codounis (1962) has also studied honey crystallization in relation to composition. In his view, the index (Brix minus dextrose) \div dextrose is more useful than other indices, including D/W . Examination of Codounis' Table 4 shows that by 'Brix' he means total solids, or 100 minus water content. Thus, either the Codounis or Austin index can be calculated from the other,* and they are thus of equal value in predicting granulation, in spite of Codounis's statement to the contrary. It should be noted that the values in Table 6.72/1 are calculated from true dextrose values and not from those obtained by the nonspecific hypiodite or other method without prior removal of interfering sugars. Codounis has noted, and we concur, that as a rough rule it can be taken that honeys with less than 30% dextrose rarely if ever granulate. Siddiqui (1970) was unable to relate granulation (as determined by the method of White *et al.*) with any of the ratios L/D , $(D-W)/L$, or D/W for 95 samples of Canadian honey in which sugars had been determined by paper chromatography. No data have been published; possibly the relative inaccuracy of the paper-chromatographic method obscured the relationship. Siddiqui further

* Codounis index = $(100/D) - (1/\text{Austin index}) - 1$

states that 'such predictions were, of course, not possible because the factor actually involved is the presence or absence of appropriate crystal nuclei'. Apparently Siddiqui failed to appreciate that nuclei are eliminated in the method of White *et al.*, as a result of the requirement that samples are heated to clarity (as indicated by the polariscope) before an undisturbed six months' storage. Presence or absence of nuclei certainly influences the onset of crystallization, but its extent and speed are dependent on the D/W ratio.

Now that a rapid and accurate photometric method is available for determination of true glucose in honey (White, 1964b), the use of D/W ratios for prediction of granulating tendency should become practical.

6.8 HYGROSCOPICITY

Because of its nature as a highly concentrated sugar solution, honey is remarkably hygroscopic for a natural product. Interest in this property arises for two reasons. First, honey absorbs moisture from the air under certain conditions, and thus becomes diluted, and more liable to fermentation. Secondly, honey can impart the desirable property of softness or non-drying to food products in which it is incorporated.

When honey is exposed to air, a gain or loss in its moisture content will take place, depending upon the temperature, the moisture content of the air, and the vapour pressure of water in the air, which is usually expressed as relative humidity.

For each honey a relative humidity exists at which no gain or loss of moisture takes place; this is the equilibrium relative humidity. It will vary with moisture content of the honey and with the gross composition, the latter having only a minor influence. Because of the high viscosity of honey, moisture absorbed at the surface can diffuse only very slowly throughout the mass, so there may be a relatively rapid dilution at the surface. The great density differences between honeys of different moisture contents also favour the maintenance of a dilute layer at the surface, rather than dispersion of absorbed moisture throughout the mass. For example, Martin (1958) has shown that within 7 days a honey sample at 22.5% moisture exposed at 86% R.H. had 26% moisture at the surface, whereas 2 cm below the surface no change was found; after 24 days the moisture content at the surface was 29.6%; at 2-cm depth it was 23.0%; at 6-cm depth no change was evident even after 95 days. Containers were 5.5 cm in diameter.

When honey is exposed to a relative humidity lower than its equilibrium value, drying will take place. Martin (1958) noted that moisture loss was more rapid at intermediate values (20-40% R.H.) than at 0% R.H. He ascribed this to the formation of a dry film on the surface which

retards further evaporation. Dyce (1931a), Nico l(1937), Hansson (1942), and Villumstad (1951) have examined the ability or inability of certain types of screw-cap containers to prevent passage of moisture into honey contained in them.

Table 6.8/1 shows the relation between equilibrium relative humidity of a clover honey and its water content.

Table 6.8/1
Approximate equilibrium between relative humidity of air and the water content of a clover honey*

| <i>Relative humidity (%)</i> | <i>Water content (%)</i> |
|------------------------------|--------------------------|
| 50 | 15.9 |
| 55 | 16.8 |
| 60 | 18.3 |
| 65 | 20.9 |
| 70 | 24.2 |
| 75 | 28.3 |
| 80 | 33.1 |

* Interpolated from the data of Martin (1958).

Hansson (1942) noted that although the water vapour pressure of honey between 10° and 40°C (50° and 104°F) corresponded in general to 60° R.H., at about 30°C it appeared to correspond to about 75% R.H. He concluded that the decrease in water content of nectar in the hive to the values normally found for honey is purely a physiochemical phenomenon. Contrary to Hansson, Bartlett (1962) found that honey containing 18% water, in a closed system, maintained a R.H. of 59 ± 4% regardless of temperature, between 4-43°C (40-100°F). Advantage of this was taken in rearing and shipping certain insect parasites and predators that can be fed on honey.

6.9. COLLOIDAL PROPERTIES AND SURFACE TENSION

6.91 Honey colloids

As previously mentioned, honey contains small amounts of colloiddally dispersed material. Probably the most extensive work with honey colloids is that of Lothrop and his colleagues (Lothrop & Paine, 1931a; Paine, Gertler & Lothrop, 1934). They reported that the colloiddally dispersed material in honey showed an isoelectric point of 4.3, being

positively charged at more acid pH values and negative in less acid honeys. Flocculation by colloids of opposite charge was demonstrated (Lothrop & Paine, 1931a), and the colloid content of various honey types was determined by ultrafiltration (Paine *et al.*, 1934). The nitrogen content of the material indicated about 55-65% protein; in the samples of lower colloid content, 15-25% was found to be fat-soluble and to resemble beeswax.

Turbidity of honey becomes more pronounced upon dilution, as the peptizing effect of the sugars on the colloidal material is reduced. If dilution is carried out near the isoelectric point, pronounced flocculation may occur. Reconcentration of honey which had been diluted to less than 10% solids does not entirely reverse the aggregation process, but when the solid content exceeds 20% the turbidity begins to decrease (Paine *et al.*, 1934). Removal of the colloidal material, by flocculation with bentonite and filtration, produces a clear honey that shows minimal Tyndall effect.

Roughly half of the nitrogen content of honey is removed by ultrafiltration, and the colour is reduced somewhat. Viscosity is decreased by only a minor amount (Paine *et al.*, 1934). 'Dextrin' content, determined by alcoholic precipitation, is not affected (Paine *et al.*, 1934).

6.92 Surface tension

Surface tension of honey is an important property; in processing of honey, a low value may lead to excessive foaming and scum formation. Paine *et al.* (1934) examined 25% solutions of 7 floral honeys and 1 honeydew honey. They found that at 20° ultrafiltration produced an average change in the surface tension from 47.0 to 60.2 dyne/cm; they noted an accompanying decrease in foaming and retention of air bubbles.

It has been noted that the thixotropic properties of heather (*Calluna vulgaris*) honey are due to gel-sol-gel transformation of a protein contained therein. Removal of the protein produced a true Newtonian liquid; addition to a clover honey made it thixotropic (Pryce-Jones, 1953, page 160). Mitchell and his colleagues (Mitchell, Donald & Kelso, 1954, Mitchell, Irvine & Scoular, 1955, Kirkwood, Mitchell & Smith, 1960, Kirkwood, Mitchell & Ross, 1961) have done extensive analyses of heather honey and proposed an analytical index to distinguish between heather honey and honeydew honey.

6.10 ELECTRICAL CONDUCTIVITY

Very little research on this property of honey has been recorded. Vorwohl (1964) cites Elser's (1924) interest. Stitz & Szigvárt (1931b) measured the conductivity of several honeys at 50% solution at 20.5C (68.9°F)

and found values ranging from 0.868 to 3.645×10^{-4} /ohm cm. In general, values increased with ash content. The effect of temperature and concentration was examined; a maximum value was generally found at between 30 and 35% solids. Vorwohl (1964) found maximum values at 20–25% solids, with values for undiluted honey around 10^{-6} to 10^{-7} /ohm cm, approaching the values for distilled water. He measured the conductivity of 40 single-species* samples of honey. His values for a 20% solution ranged from 0.85 to 8.47×10^{-4} /ohm cm. Other samples ranged from 0.6 to 1.46 for floral honeys (heather 7.7) and from 6.3 to 16.41 for honeydew honey. He proposed the use of conductivity with pollen analysis for identifying honey sources and for determining the proportion of honeydew honey. Kaart (1961) proposed the measurement of electrical conductivity as more rapid than chemical analysis for determining suitability of honey for winter stores for bees.

Conductivity values will depend on the concentrations of mineral salts, organic acids, proteins, and possibly complexing materials such as sugars and polyols.

6.11 FERMENTATION

The discussion here is limited to undesired or spoilage fermentation of honey. Section 10.3 discusses methods for preventing undesired fermentation, and Chapter 16 describes controlled fermentation to produce alcohol.

Much of our present knowledge of undesirable honey fermentation dates from the late 1920s and early 1930s, when several groups of investigators in the northern U.S. and Canada (Fabian & Quinet, 1928, Marvin, 1928, Lochhead & Heron, 1929, Wilson & Marvin, 1929, Lochhead & Farrell, 1930a, 1930b, 1931a, 1931b, Marvin, 1930, Marvin *et al.*, 1931, Wilson & Marvin, 1931, Dyce, 1931, Wilson & Marvin, 1932, Lochhead, 1933) studied the problem. Loss and damage to commercial honey was extensive in these areas; an understanding of the factors involved soon led to adequate control methods.

6.11.1 Yeasts and moisture content

It is generally agreed that all honeys contain osmophilic (sugar-tolerant) yeasts in greater or lesser amount, and will ferment if the moisture content is high enough, and the storage temperature suitable, if granulation occurs, if the yeast count is high enough in relation to the moisture content, and if ash and nitrogen contents are favourable.

Numerous strains of these sugar-tolerant yeasts have been isolated

* The samples were obtained experimentally from small colonies caged upon various plantings (Z. Denianowicz, 1964).

from fermenting honey. Table 6.11.1/1 lists those most frequently encountered. The sources of the yeasts have received some attention. Fabian & Quinet (1928) reviewed the earlier literature (from 1884) on the micro-organisms, including yeasts, in nectars. Lochhead & Heron (1929) isolated numerous osmophilic yeasts from nectar. These yeasts also may enter honey from the body of the bee (Klöcker, cited by Fabian & Quinet, 1928) apiary soil (Lochhead & Farrell, 1930a), and honey-house air and equipment (Lochhead & Farrell, 1931b).

Table 6.11.1/1
Yeasts isolated from honey

| Type | Reference |
|---------------------------------------|---------------------------|
| <i>Nematospora ashbya gossypii</i> | Aoyagi & Oryu, 1968 |
| <i>Saccharomyces bisporus</i> | " " " " |
| " <i>torulosus</i> | " " " " |
| <i>Schizosaccharomyces octosporus</i> | Lochhead & Farrell, 1931b |
| <i>Schwanniomyces occidentalis</i> | Aoyagi & Oryu, 1968 |
| <i>Torula mellis</i> | Fabian & Quinet, 1928 |
| <i>Zygosaccharomyces</i> spp. (2) | Nussbaumer, 1910 |
| " <i>barkeri</i> | Lochhead & Heron, 1929 |
| " <i>japonicus</i> | Aoyagi & Oryu, 1968 |
| " <i>mellis</i> | Fabian & Quinet, 1928 |
| " <i>mellis acidi</i> | Richter, 1912 |
| " <i>nussbaumeri</i> | Lochhead & Heron, 1929 |
| " <i>priorianus</i> | Fabian & Quinet, 1928 |
| " <i>richteri</i> | Lochhead & Heron, 1929 |

It has frequently been recorded that fermentation—when it does occur—almost invariably follows granulation of honey. The removal of dextrose hydrate from solution leaves a higher-moisture liquid phase in which moisture may not be uniformly distributed. In the moisture range found in honey, a small increase in moisture can produce a considerably increased liability to fermentation. In partly granulated fermenting honey, the higher moisture content in surface layers may also result from absorption of moisture from the air above.

In his study of the hygroscopicity of honey, Martin (1958) made yeast counts at different depths of the exposed samples. In honey originally containing about 700 000 cells/g, exposed to 66% R.H., where the surface moisture did not exceed 21.5% only very limited aerobic (and no anaerobic) growth took place. The same honey exposed to 10% R.H. developed heavy surface growth within 17–30 days (at which time surface

moisture values were 28-29%), though anaerobic growth was quite limited lower down, where moisture content remained at 22.5%. The increase of pollen content at the surface of honey when it absorbs moisture would also favour yeast growth. Krumholz (1936) has reviewed fermentations of high-density sugar solutions (including honey) and believes that there is no valid upper limit to the sugar concentration that the osmophilic yeasts can tolerate. Lochhead (1933) has summarized their investigations on the relation of moisture content and fermentation as follows, based on 319 honey samples:

| <i>Moisture content</i> | <i>Liability to fermentation</i> |
|-------------------------|----------------------------------|
| below 17.1% | safe regardless of yeast count |
| 17.1-18.0% | safe if yeast count < 1000/g |
| 18.1-19.0% | " " " " < 10/g |
| 19.1-20.0% | " " " " < 1/g |
| above 20.0% | always in danger. |

Stephen, however (1946), reported in a study of over 700 Canadian honey samples that the incidence of fermentation was greatest in samples containing 17-18% moisture; above 19%, the lowered granulation tendency indirectly retards yeast growth.

6.11.2 Storage temperature

Wilson & Marvin (1931, 1932) recommended that honey be stored either below 52°F (11°C) or above 70°F (21°C), thus defining the range favourable to fermentation. The lower half of this range is that most favourable for honey granulation. In well ripened honey, fermentation is said not to occur at temperatures above about 80°F (26.7°C) (Wilson & Marvin, 1932). Other factors must, however, be considered when thinking in terms of higher temperature storage. Honey in unheated winter storage is more liable to fermentation in the spring, since temperatures then become more favourable, and the honey will usually have granulated during the winter.

6.11.3 Products of fermentation

Fermentation in full-density honey is quite slow, extending over periods of six months to a year. Krumholz (1936) characterizes osmophilic yeasts as having slight fermenting power (50-70 g alcohol per litre) and a high tolerance to sugar concentration—the opposite of the non-osmophilic yeasts. Marvin *et al.* (1931) found that in 50% honey solution five honey yeasts completed fermentation in about 40 days and produced 4.0-5.6 g carbon dioxide, 3.8-5.0 g alcohol, and 1.5-3.1 milliequivalents of acidity, over 90% non-volatile. Borries (1934), studying natural honey fermentation, found small amounts of ethanol and CO₂ produced. Only

part of the latter is evolved; the remainder was recovered under diminished pressure. Less than 1% of the sugar was fermented, and no increase in acids could be detected.

It has since been found (Spencer & Sallans, 1956, Spencer & Sha, 1957, Peterson *et al.*, 1958, Hajny *et al.*, 1960) that various osmophilic yeasts isolated from honey can, under suitable conditions, convert 60% of a 10-20% glucose solution to polyols, such as glycerol, D-arabitol, erythritol and mannitol. In fermenting 20% glucose solution, aeration and low phosphate content favour the production of the polyols, whereas in the absence of aeration the production of ethanol is increased and of polyols is greatly reduced. It appears unlikely that polyols would be produced during natural fermentation of honey.