Heats of combustion of the main carbohydrates contained in plant-source foods

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In a previous review, the experiments of American chemist W.O. Atwater were critically examined, with the findings demonstrating certain weaknesses that could compromise the validity of the values currently used for metabolizable energy. An examination of published works on the heat of combustion of carbohydrates reveals 2 types of weaknesses: the inaccuracy and imprecision of the calorimetric data used, and the averaging procedure employed to estimate such representative values. The present review focuses on the first type of weakness, namely the inaccuracy and imprecision of the calorimetric data used in previous studies. An exhaustive bibliographic search yielded almost 100 heat of combustion values for some of the 6 main carbohydrates contained in plant-source foods (glucose, fructose, sucrose, maltose, starch, and cellulose). These heats of combustion were subjected to rigorous statistical analysis to propose the following for each carbohydrate: (1) an interval (termed a bibliographic interval) that very likely includes the actual heat of combustion value and (2) a "representative value" (calculated to produce the minimum level of inaccuracy). In addition, an estimation of the maximum level of inaccuracy that could be expected when using such a representative value is reported.

INTRODUCTION

The successful implementation of nutritional strategies designed to prevent or treat degenerative chronic diseases usually requires precise knowledge of the metabolizable energy value (ME) attributable to each macronutrient (ME_m, in which m can denote carbohydrates [c], proteins [p], or lipids [l]). The ME_m values currently in use are those published by W.O. Atwater in 1910[1]: $ME_c = 4$ kcal/g, $ME_p = 4$ kcal/g, and $ME_l = 9$ kcal/g. More than a century later, updating these values may be critically important for the

continued development of nutrition science. A review published in 2017[2] presented an exhaustive critical analysis of the experiments conducted by Atwater and his colleagues[3–14] to obtain ME_m values. In that review, substantial deficiencies that could compromise the validity of the metabolizable energy values currently in use were identified.

The main objective of this review is to estimate, by means of an exhaustive bibliographic review, the representative values for the heats of combustion for each of the 6 main types of carbohydrates contained in plant-source foods (glucose, fructose, sucrose, maltose, starch,

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and cellulose). An additional aim is to assess the levels of inaccuracy and imprecision that may be expected for each of these values.

BACKGROUND ABOUT THE HEAT OF COMBUSTION IN CARBOHYDRATES

Atwater[7] proposed that the metabolizable energy value attributable to carbohydrates can be calculated as follows: $ME_c = HC_c \; A_c$, where HC_c is the heat of combustion produced by each gram of carbohydrate and A_c is the availability coefficient of the carbohydrate (the fraction of the heat producible by the combustion of the ingested carbohydrate that the human body is truly capable of producing and using for its organic functions). Atwater and Bryant[8] proposed the following values for the A_c parameter: cereals, 0.98; legumes, 0.97; vegetables, 0.95; and fruits, 0.90. Because these values are very close to 1.0, the level of accuracy and precision of the ME_c value for a given sample could be expected to depend highly on the level of accuracy and precision of the corresponding HC_c value.

A critical analysis of the procedure used by Atwater and Bryant[8] to propose their HC_c values (4.2 kcal/g for carbohydrates contained in plant-source foods or 3.9 kcal/g for carbohydrates contained in animal-source foods) reveals 2 types of general deficiencies: the inaccuracy and imprecision of the calorimetric data used to calculate their HC_c values, and the averaging procedure used to estimate such values.

Inaccuracy and imprecision of the calorimetric data

With regard to experimental errors, is noteworthy that, when Atwater and Bryant[8] published their proposal to estimate the HC_c values, they never presented an analysis of the level of imprecision or inaccuracy of their calorimetric values. However, in a subsequent paper, Atwater and Snell[15] published an analysis of the random experimental errors attributable to Atwater's measurements, affirming that the estimated errors were usually less than 0.5%. Nevertheless, when estimating this value, only the failures occurring during the calorimetric experiments were taken into account, excluding those caused by the following: impurities present in the samples characterized; the level of inaccuracy of the heat of combustion value assigned to the corresponding reference material (which is used as a calibration standard; the experimental measurement shows a direct relationship with this value); and the incomplete combustion of samples. Clearly, the effect of these failures may be considerably more important than the effects of the errors estimated by Atwater and Bryant.[15] In addition, using only the data in Atwater and Bryant's paper on this topic,[8] it cannot be determined with certainty whether the heat of combustion values used to calculate the HC_n values were measured experimentally by Atwater himself or were collected from previous studies. Consequently, the applicability of the error estimation presented by Atwater and Bryant[15] remains uncertain.

In light of these circumstances and in order to evaluate the possibility of additional sources of error, it would be useful to examine some specific physicochemical characteristics of the experimental system. To do this, it is important to note 4 key factors. (1) In a given carbohydrate sample, the presence of a miniscule amount of lipid, protein, or both is very probable. Thus, since the heat of combustion values of lipids and proteins are noticeably higher than those characterizing carbohydrates,[2] overlooking the presence of these substances in carbohydrate samples may produce an overestimation of the HC_c value, which increases as the contaminant content increases. (2) Carbohydrates are usually hygroscopic at a certain level. Since the water absorbed by carbohydrates does not produce energy during the combustion process but its presence modifies the sample weight, the heat of combustion by gram estimable from a particular wet sample decreases as its water content increases (referred to herein as the *diluent effect*). In addition, when the water content of a carbohydrate sample is comparatively high, attaining complete combustion may become difficult. (3) Since the 19th century, benzoic acid, naphthalene, and sucrose have been used as reference materials to measure heats of combustion.[16–19] However, the incidental presence of impurities or moisture in such materials (mainly as consequence of their handling in situ) results in an inaccurate assignation of the heat by gram produced during combustion of these materials, thereby generating an inaccurate value of the sample's heat of combustion. (4) The ash produced at the end of an incomplete burn process is usually a mixture of substances that may be chemically different from the original sample (eg, mixtures containing carbon, other partially oxidized organic compounds, mineral oxides, and unburned sample). Therefore, it is reasonable to expect that, during this partial oxidation, a certain amount of energy will be consumed or produced.

With regard to the inaccuracies associated with ash production, it is noteworthy that, when it is arbitrarily assumed that no ash is formed (eg, when the presence of ash is consciously ignored) and the heat produced by a given sample is attributed to the total sample (here named *assumption A*), the heat of combustion by gram is slightly underestimated. Thus, a more accurate alternative would be to assume that the heat produced during the combustion process is attributable solely to the

mass being completely burned (eg, the weight calculated by subtracting the residual ash weight from the initial sample weight, here named *assumption B*), which implicitly considers that the ash consists of completely unreacted sample. It is nonetheless possible that an incomplete combustion process can produce at least a portion of the ash. It would thus be logical to assume that assumption B is still slightly inaccurate. Nevertheless, in cases in which the exact composition of the ash is unknown, this assumption could be considered as an acceptable option.

Atwater's averaging procedure

The averaging procedure applied by Atwater and Bryant[8] to the available heat of combustion values for carbohydrates was critically analyzed in a previous review[2] and found to have significant deficiencies. However, since the relative content of the different carbohydrate types contained in several plant-source foods is currently known,[20] such an averaging process may be unnecessary when representative values for the heats of combustion of those carbohydrate types are available. This is because the heat produced by a combustion process is an additive property, meaning that it can be obtained by adding the energy produced by each type of component. The heat of combustion produced by each gram of the carbohydrate mass contained in a given food ($HC_{c\ in\ f}$; expressed in kcal/g of carbohydrate in such food) can thus be estimated using equation 1:

$$HC_{c\ in\ f} = 0.01[(\bar{C}_1)(HC_1) + (\bar{C}_2)(HC_2) + (\bar{C}_3)(HC_3) + (\bar{C}_4)(HC_4) + (\bar{C}_5)(HC_5) + (\bar{C}_6)(HC_6)]$$

(equation 1)

where, $\bar{C}_i$, is the mean percent composition reported for the respective carbohydrate *i* in a given food (*i*: 1 [= glucose], 2 [= fructose], 3 [= sucrose], 4 [= maltose], 5 [= starch] or, 6 [= cellulose]),[20] and HC_i is the representative value for the heat of combustion of the corresponding carbohydrate.

BIBLIOGRAPHIC ESTIMATE OF THE HEATS OF COMBUSTION

Literature search

With the aim of finding the most accurate available estimation of representative values for the heats of combustion of the carbohydrates contained in plant-source foods, an exhaustive bibliographic search was performed for the current review. This search began with a book published in 1979 by the world-renowned

International Union of Pure and Applied Chemistry, Physical Chemistry Division.[16,21] This volume included a review that cited calorimetric data for certain carbohydrates.[22] In that review, numerous authors who had worked to determine the heat of combustion values for carbohydrates were mentioned (eg, M. Berthelot, F. Stohmann, M. Rubner, C. von Rechenberg, W.O. Atwater, E. Fischer, F. Wrede, T.W. Richards, and E.S. Domalski). An online search for publications by these authors on this topic was conducted as extensively as possible, and any relevant information was recorded.

A comprehensive analysis of the available information revealed 4 deficiencies, described here. (1) In several cases, the original bibliographic sources were improperly cited or even omitted (it was a very common practice to include a "citing reference" instead of citing the original source). (2) When several data were available for the purportedly same substance, the original values were generally not reported; instead, only a representative value was provided, often obtained after an arbitrary and frequently undescribed averaging procedure. (3) No general rule existed to define the number of decimal places used to report a given datum, particularly in the case of earlier papers. (4) As a consequence of the different definitions for the standard calorific unit (calorie), as well as the different heat of combustion values reported for the reference materials used throughout years,[16–18,23–25] some authors of citing references reported corrected values instead of the original values.

With regard to the above-mentioned deficiencies (3) and (4), it should be noted that, when 2 or more so-called citing references report the same original datum, the use of a different number of decimal places or the reporting of corrected data instead of the original data (without providing precise and sufficient information about the correction procedure used) or both creates a situation in which a single datum could be interpreted as 2 or more individual data. In the current review, the occurrence of this deficiency was minimized as much as possible. The 4 above-mentioned deficiencies would, on their own, underscore the critical need to conduct a thorough data compilation, considering the original sources as far as possible. Moreover, in order to identify possible experimental errors and to estimate the accuracy levels of the reported data, both of which are among this review's main objectives, a careful analysis of the full texts of the different original papers is essential.

To this end, a retrospective analysis of the original sources was performed. In addition to the publications cited directly in the review articles,[16,21,22] the bibliographic citations of other useful calorimetric data collections[26–29] and the names of additional authors reporting calorimetric data for carbohydrates were

identified. To the greatest extent possible, these published papers were also obtained and analyzed.

Finally, an internet search was performed that included all combinations of the different known names of the carbohydrates of interest (eg, glucose, dextrose, fructose, levulose, sucrose, cane sugar, maltose, starch, and cellulose) and the following keywords: heat, combustion, calorimetry, and calorimeter. In this process, some authors who recently reported data of interest were identified. However, the most valuable result of the search was the obtainment of data sheets with calorimetric information published by the National Institute of Standards and Technology.[30–33] During this bibliographic search, several previously identified references were cited, but a few other references were also obtained.

Bibliographically obtained data

As a result of the above-described search, almost 100 heats of combustion reported over more than a century were collected.[8,15,19,22,26–29,33–53] Nonetheless, deficiencies related to the citing information, the current inaccessibility of the original works (mainly because of the age of such works), or both prevented approximately 40% of the available data from being collected from the original sources; instead, such data had to be obtained from one or more citing references.[15,19,22,26–29,34–37, 39,40,44] In addition, there were a few data that had been collected from references considered to be original references, but it is not clear whether these data were obtained from previous papers (no references were cited) or derived from experiments conducted by the paper's authors (no experimental procedure was included in these papers).

Thus, for data obtained from an original reference, the correspondent mean value ($\bar{X}$) and, when available, the standard error of the mean (se), the number of data (n), and the number of different samples characterized (m) will be reported; the m value will be presented only when the use of 2 or more clearly differentiated samples was explicitly indicated by the corresponding authors. Finally, in an effort to achieve some level of congruence with the respective authors, the $\bar{X}$ and se values in this work were presented with the same number of decimal places as the original data used to calculate them. Otherwise, for each datum obtained from a citing reference, only the corresponding mean value ($\bar{X}$) and a sequential identifier designated by a Roman numeral inside parentheses were presented; the latter identifier is required to suitably read the additional information presented in Table 1.[15,19,22,26–29,34–37,39,40,44]

The collected data were statistically analyzed with the aim of proposing an interval for each carbohydrate, within which it would be very probable to find the actual heat of combustion value for the carbohydrate in question (hereafter referred to as the *bibliographic interval*). In addition, for each carbohydrate, a representative value was proposed that could be recommended to be used when obtaining a reference value is the primary focus of interest.

Categorization of the estimated degree of imprecision for the available data

An important goal of this work is to determine the degree of imprecision of the available data. First, to estimate the relative relevance of the published data (data categorization), the available bibliographic reports were classified by taking into account the estimated level of precision of their data by qualitatively defining the following 3 levels:

(L-I) This level is assigned to studies that include, or for which critical review(s) of them include, data that either determine or would lead one to infer that one or more of the following errors occurred when determining the reported value: (1) use of sample(s) containing impurities whose effect on the heat of combustion value was not considered; (2) use of calculations showing that some energy interchange(s) occurring in the system were not (or could have not been) precisely considered; (3) inappropriate assignment of the heat of combustion characterizing the reference material used; or (4) performing of some action during the experimental or calculating procedure that compromised the accuracy of the reported datum.

(L-II) This level is assigned to data published or cited in a paper that did not have sufficient information to confirm or rule out the presence of impurities or the existence of any other experimental error that could compromise the accuracy of the reported data.

(L-III) This level is assigned to studies that may be classified into at least one of the following subgroups: (1) The substance characterized in the study has been explicitly declared by the authors as being free of contaminants and water and was completely burned during combustion (ash free). In addition, no evidence exists to support the claim that other experimental error or miscalculation was involved. (2) The value reported in the study was corrected by the original authors (or it was made available to be corrected in the present work) in order to represent the behavior of a hypothetical substance that was free of contaminants and water and was completely burned. When correcting the data, the following information was considered: (a) the heat of combustion value reported for the impure sample; (b) the heat produced by the mass of contaminant(s)

Table 1 Additional information about the citing references, labeled in Tables 2 through 7 (Roman numerals shown in superscript in Tables 2 through 7 refer to the identifiers shown here)

Identifier	Additional information
(I)	Kharasch (1929)[27] considered this value to be imprecise
(II)	Kharasch (1929)[27] and Domalski (1972)[29] attribute this value to the following publication: Emery & Benedict. *Am. J. Physiol.* 1911;28:301–307; in Kharasch (1929),[27] this value was considered imprecise
(III)	Fries (1907)[26] and Domalski (1972)[29] attribute this value to a datum in a paper by C. von Rechenberg, probably published in 1880. Rubner (1885)[35] and Stohmann (1885)[36] both considered this datum to be inappropriately overestimated; therefore, in the present review it was classified in group L-l. Moreover, it was considered an outlier by the statistical analysis performed in the present review
(IV)	Domalski (1972)[29] and Karrer et al (1921)[44] attribute this value to a publication by Keller (1921)
(V)	Huffman & Duncan (1944)[28] attribute this value to a paper by C. von Rechenberg (probably published in 1880)
(VI)	Huffman & Duncan (1944)[28] attribute this value to the following publication: Mitchell HH, Hamilton TS, Haines WT. *J Agric Res.*1940;61:847–864
(VII)	Cox & Pilcher (1970)[22] and Domalski (1972)[29] attribute this value to the following publication: Ponomarev VV, Alekseeva TA. *Zhur Fiz Khim*. 1961;35:1629–1633
(VIII)	Cox & Pilcher (1970)[22] and Domalski (1972)[29] attribute this value to the following publication: Skuratov SM, Strepikheev AA, Kozina MP. *Doklady Akad Nauk SSSR*. 1957;117:452–454
(IX)	Cox & Pilcher (1970)[22] and Domalski (1972)[29] attribute this value to the following publication: Ponomarev VV, Migarskaya LB. *Zhur Fiz Khim*. 1960;34:2506–2508
(X)	Huffman & Duncan (1944)[28] attribute this value to a paper by E.F. DuBois, published in 1927
(XI)	Fries (1907)[26] attributes this value to a paper by M. Berthelot
(XII)	Huffman & Duncan (1944)[28] attribute this value to a paper by L.A. Maynard, published in 1937
(XIII)	Fries (1907),[26] Huffman & Duncan (1944),[28] and Gibson (1891)[39] attribute this value to a paper by M. Berthelot & P. Vieille
(XIV)	Berthelot & Vieille (1887)[37] attribute this value to a paper by C. von Rechenberg (probably published in 1880) and provide information to question the precision of the corresponding data; therefore, Rechenberg's data were classified in the L-I group
(XV)	Fries (1907)[26] attributes this value to a paper by F. Stohmann
(XVI)	Dickinson (1915)[19], Kharasch (1929),[27] and Rubner (1885)[35] attribute this value to the following publication: Fisher E, Wrede F. *Z Phys Chem*. 1909; 69:218
(XVII)	Dickinson (1915)[19] and Domalski (1972)[29] attribute this value to the following publication: Wrede F. *Zeit Phys Chem*. 1910; 75:81
(XVIII)	Atwater & Snell (1903)[15] and Fries (1907)[26] attribute this value to Tower
(XIX)	Rubner (1885)[35] attributes this value to the following publication: Fisher E, Wrede F. Sitzber *Preuss Akad Wiss Physik Math Kl*. 1904; p 687
(XX)	Fries (1907)[26] attributes this value to a paper by Danilewsky
(XXI)	Huffman & Duncan (1944)[28] attribute this value to a paper by Y. Nakamura, published in 1935
(XXII)	Huffman & Duncan (1944)[28] attribute this value to the following publication: Fingerling G, Köhler A, Reinhardt F. *Landw Vers Sta*. 1914;84:149–230
(XXIII)	Huffman & Duncan (1944)[28] attribute this value to the following publication: Kellner O, Köhler A. *Landw Vers Sta*. 1900;53:1–474
(XXIV)	Huffman & Duncan (1944)[28] attribute this value to a paper by Loewy
(XXV)	Fries (1907)[26] attributes this value to a paper by F. Stohmann and H. Langbein
(XXVI)	Karrer et al (1921)[44] attribute this value to a paper by Keller, published in 1921
(XXVII)	Berthelot & Vieille (1885)[34] attribute this value to a paper by P. Vieille and E. Sarrau
(XXVIII)	Stohmann (1885)[36] attributes this value to a paper by M. Berthelot
(XXIX)	Fries (1907),[26] Kharasch (1929),[27] Berthelot & Vieille (1885),[34] Stohmann (1885),[36] Stohmann & Langbein (1892)[40] attribute this value to the following publication: Gottlieb. *J Prakt Chem*.1883;2:385
(XXX)	Fries (1907)[26]attributes this value to a paper by M. Berthelot & P. Vieille.

reported for each sample (the following heat of combustion values were considered: protein, 5.8 kcal/g[8]; lipids, 9.3 kcal/g[8]); (c) the water diluent effect; and (d) the amount of ash produced by the sample (it was assumed that ash formation is a thermally inert process, meaning that it neither produces nor consumes heat; this implies that assumption B was deemed suitable). (3) The value reported in the study is an average value of measurements for a set of samples obtained from different sources or using clearly different purification procedures; however, the corresponding values are very close (eg, their standard deviation is less than 0.05% of their average value).

STATISTICAL ANALYSIS

Before starting a statistical analysis, it is essential to determine the presence of outlier data, which are data that seem to be inconsistent with the rest of the data. The boxplot is a practical tool for identifying possible outlier data.[54] An experimental value is considered an outlier if it falls outside the interval: $[Q_1 - k(IQR), Q_3 + k(IQR)]$,

where Q_1 is the lower quartile of the data set, Q_3 is the upper quartile, and IQR = Q_3 – Q_1 (interquartile range). When defining such an interval,[54] the use of k = 3.0 could be considered to be a conservative decision, which reduces the possibility of unnecessarily eliminating a datum (only around of 0.2% for n = 100[54]); hence, in the present review, this value was used for k.

For sets with few data (eg, between 4 and 6), an alternative method is Grubbs' test,[55] which can be used when only one value is suspected to be an outlier datum. For example, if the maximum value of a set with few data is suspected to be an outlier datum, the following comparison must be done:

$$\frac{(X_{max} - \bar{X})}{S} > G \qquad \text{(equation 2)}$$

where $\bar{X}$ is the mean of the n available data (including the X_{max} value), S is an estimation of the population standard deviation (calculated on the basis of all sample data), which must be calculated with $n - 1$ degrees of freedom, and G is a special critical value for a one-sided test. The G value depends on the significance level α, the sample size n, and the critical value of the t distribution with $n - 2$ degrees of freedom and a significance level of α/n.[55,56] When this criterion of inequality is met, the X_{max} value can be considered an outlier datum.

After excluding the outlier data, the weighted mean of the sample ($\bar{X}_w$) was calculated with equation 3.[57]

$$\bar{X}_w = \frac{\sum_{i=1}^{k} w_i x_i}{\sum_{i=1}^{k} w_i} \qquad \text{(equation 3)}$$

In equation 3, x_i denotes each one of the mean values of the respective data sets, and w_i represents a set of weighting factors. Because of the lack of information provided in the most of the available papers, weighting factors commonly used in literature[57,58] cannot be used here. Thus, as an alternative option that would allow a slightly superior relevance to be assigned to those data published in papers that were categorized as having a higher level of precision (eg, L-III > L-II > L-I), the following 3 sets of weighting levels (w_i values) were tested: (a) for L-III, 2.0; for L-II, 1.0; and for L-I, 0.5; (b) for L-III, 1.5; for L-II, 1.0; and for L-I, 0.67; and (c) for L-III, 1.25; for L-II, 1.0; and for L-I, 0.8.

With regard to variance, when the weighting factors are not frequencies, as in the previously mentioned options, the unbiased estimation of the sample standard deviation can be calculated using the following equation[58]:

$$S_w = \sqrt{\frac{\sum_{i=1}^{k} w_i (x_i - \bar{X}_w)^2}{\sum_{i=1}^{k} w_i - \left(\sum_{i=1}^{k} w_i^2 \middle/ \sum_{i=1}^{k} w_i \right)}} \qquad \text{(equation 4)}$$

Since the differences among the results obtained with each of the weighting levels were not considered relevant, only the results obtained with weighting level (b) are presented in this work. As a typical example, the results for glucose were as follows: For the set of weighting levels (a): $\bar{X}_w = 3.732$ and $S_w = 0.023$; for the set of weighting levels (b): $\bar{X}_w = 3.733$ and $S_w = 0.023$; and for the set of weighting levels (c): $\bar{X}_w = 3.733$ and $S_w = 0.023$.

Since the present work aims to propose intervals (1 for each carbohydrate) for the heat of combustion with a high probability of including the actual heat of combustion value (HC), the following interval (named the *bibliographic interval*) is proposed[59]:

$$\bar{X}_w - h\, S_w \leq HC \leq \bar{X}_w + h\, S_w \qquad \text{(equation 5)}$$

where h is a statistical factor that depends on the N value (total number of experimental data corresponding to each carbohydrate), the desired level of distribution coverage (here, a coverage of 90% was selected), and the defined confidence level (in this review, 90%, assuming a 2-tailed distribution).[59] Since several authors did not report the sample size, the exact N value remains unknown, but by analyzing the available information for each carbohydrate, it is very probable that $15 \leq N \leq 200$. If $N = 15$, then $h = 2.28$, and if $N = 200$, then $h = 1.76$[59]; therefore, the use of $h = 2$ for all carbohydrates was considered an acceptable approximation. On the basis of the above-mentioned data, the proposed interval for glucose would be as follows: $3.733 - 2(0.023) \leq HC \leq 3.733 + 2(0.023)$ or, alternatively, $HC = 3.733 \pm 0.047$; the respective bibliographic intervals are presented in Tables 2 through 7[8,15,19,22,26–29,33–54] at the end of the data set considered for each type of carbohydrate.

RESULTS

Tables 2 through 7 contain the bibliographic data categorized as previously indicated, with each table presenting data for each type of carbohydrate as follows: Table 2,[26,27,29,40,41,44–46,49] maltose; Table 3,[8,27,29,40,41,49] fructose; Table 4,[8,22,26–29,36,38–41,46,48,53] glucose; Table 5,[8,15,19,22,26,27,29,35–37,39–43,45–47,51,54] sucrose; Table 6,[8,26–28,36,37,39–42,44–46,50,51,53,54] starch; and Table 7,[8,26,27,33,34,36,37,40,41,43,45,46,52,54] cellulose. In the heading of each table, the different names

Table 2 **Heat of combustion values and bibliographic intervals for (A) crystallized maltose and (B) anhydrous maltose[a]**

(A) Crystallized maltose: Kharasch (1929),[27] Stohmann & Langbein (1892)[40]
(Mono)hydrated maltose: Fries (1907)[26]
β-maltose monohydrated: Domalski (1972),[29] Clarke & Stegeman (1939)[49]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
3.7218 ± 0.0018(I) Stohmann & Langbein (1892)[40] 3.73(II)b **3.932(III)**	4	2	No data available			3.77778 ± 0.00012b Clarke & Stegeman (1939)[49]	8	2
						Bibliographic interval: 3.753 ± 0.067		

(B) Maltose: Fries (1907),[26] Kharasch (1929),[27] Domalski (1972),[29] Wiley & Bigelow (1898),[41] Karrer & Fioroni (1922),[45] Karrer &Fioroni (1923)[46]
Anhydrous maltose: Stohmann & Langbein (1892),[40] Karrer et al (1921)[44]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
3.9493 ± 0.0022(I) Stohmann & Langbein (1892)[40] 3.950 Wiley & Bigelow (1898)[41] **4.163(III)b**	3		3.949 Karrer & Fioroni (1923)[46] 3.949 Karrer & Fioroni (1922)[45] 3.949(IV)b			No data available		
						Bibliographic interval: 3.949 ± 0.001 (3.98 ± 0.07)[c]		

[a]Bold values indicate data that were considered outliers after the methods described in the Statistical Analysis section were applied.
[b]Reference cited by Domalski (1972),[29] who discredited this datum, although no supporting argument was presented.
[c]Interval estimated from data for hydrated maltose (see Discussion).

Table 3 **Heat of combustion values and bibliographic interval for fructose**

Fructose: Wiley & Bigelow (1898)[41]
d-fructose: Stohmann & Langbein (1892)[40]
β-D-fructose[a]: Kharasch (1929),[27] Domalski (1972)[29]
Levulose: Atwater & Bryant (1900),[8] Stohmann & Langbein (1892)[40]
β−d-levulose: Clarke & Stegeman (1939)[49]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
3.726(II)b 3.750 Wiley & Bigelow (1898)[41] 3.7550 ± 0.0032(I)b Stohmann & Langbein (1892)[40]	3		3.76 Atwater & Bryant (1900)[8]			3.73226 ± 0.00016 Clarke & Stegeman (1939)[49]	6	2
						Bibliographic interval: 3.743 ± 0.030		

[a]Kharasch (1929)[27] named the substance l-fructose, citing Emery(II) and Stohmann & Langbein (1892)[40] as his bibliographic sources. However, Domalski (1972)[29] cited the same sources and named the same substance β-D fructose. Meanwhile, in the original paper published by Stohmann & Langbein (1892),[40] the substance was named d-fructose, or levulose. Thus, in the present review, it is assumed that Kharasch (1929)[27] made a typographical error, and here, this datum is named β-D fructose.
[b]Reference cited by Domalski (1972),[29] who discredited this datum, although no supporting argument was presented.

used for each carbohydrate are shown, indicating in each case the specific references in which these names were used. In the main body of each table, the corresponding bibliographic data set is presented. Lastly, the so-called bibliographic interval, estimated considering weighting level (b), is included. Additional information about the citing references can be found in Table 1.

DISCUSSION

Tables 2 through 7 show, in bold type, the 9 data that were considered outliers after the above-described statistical methodologies were applied. In the case of crystallized maltose (Table 2, part A[26,27,29,40,49]), since only 4 data were available, Grubbs' test[55–56] was used to determine the possible existence of an outlier datum, with

Table 4 **Heat of combustion values and bibliographic interval for glucose[a]**

Glucose: Fries (1907),[26] Huffman & Duncan (1944),[28] Berthelot & Recoura (1888),[38] Karrer & Fioroni (1923)[46]
d-glucose: Kharasch (1929),[27] Stohmann & Langbein (1892)[40]
α−d-glucose: Cox & Pilcher (1970),[22] Domalski (1972),[29] Huffman & Fox (1938),[48] Kabo et al (2013)[53]
Dextrose: Atwater & Bryant (1900),[8] Fries (1907),[26] Kharasch (1929),[27] Stohmann (1885),[36] Gibson (1891),[39] Stohmann & Langbein (1892),[40] Wiley & Bigelow (1898)[41]
α-Dextrose: Huffman & Fox (1938)[48]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
3.692 ± 0.010[(I)b] Stohmann (1885)[36]	6		3.680[(VI)]			3.7200 ± 0.0002 Huffman & Fox (1938)[48]	9	4
3.739[(II)]			3.714[(VII)]	4				
3.7426±0.0030[(I)] Stohmann & Langbein (1892)[40]	5		3.717 Kabo et al (2013)[53]					
3.744 ± 0.012[b] Berthelot & Recoura (1888)[38]	5	2	3.719[(VIII)]					
3.750 Wiley & Bigelow (1898)[41]			3.721[(IX)]					
3.754 ± 0.005[b] Gibson (1891)[39]	4		3.740[(X)]					
3.939[(III)(V)b]			3.743 Karrer & Fioroni (1923)[46]					
			3.75 Atwater & Bryant (1900)[8]					
			3.760[(XI)]					
			3.760[(XII)]					
			3.762[(XIII)]					
						Bibliographic interval: 3.733 ± 0.047		

[a]Bold values indicate data that were considered outliers after the methods described in the Statistical Analysis section were applied.
[b]Domalski (1972)[29] discredited this datum without providing a supporting argument. Nevertheless, it allows one to consider that this datum could be properly classified in precision level L-I.

the result demonstrating that the higher value is an outlier. To analyze the data for fructose (5 data; Table 3) and maltose (6 data; Table 2, part B[26,27,29,40,41,44–46]), both statistical tests were used (the boxplot[54] and Grubbs' test[55,56]). The same conclusions were reached with both tests; that is, there are no outlier data in the case of fructose, and the maximum value in the case of maltose is an outlier. For the remaining types of carbohydrates, only the boxplot[54] was used. In total, only 9 outlier data were identified, which represent only 9% of the total data considered. Furthermore, most of them (6 data) were reported by the same author (C. von Rechenberg), whose work was previously criticized by Rubner and Stohmann,[35,36] who argued that the heat irradiated to the environment had been estimated inaccurately, which resulted in the reported data being considerably overestimated.

A second aspect that was analyzed is the dispersion of the bibliographic data reported for each carbohydrate, which was estimated using the coefficient of variation, defined as follows: $100 \ (S_w/\bar{X}_w)$; this coefficient is expressed as a percentage. Thus, as shown in Tables 2 through 7, such coefficients were ≤ 1.2%, which, considering the above-described potential experimental problems, can a priori be considered suitable.

A set of data that must be considered more in depth are the 5 data available for anhydrous maltose (since the datum published by Rechenberg was considered an outlier, it was not taken into account in the current review), which are surprisingly similar, especially the 3 values of 3.949 kcal/g reported by Karrer et al in 3 publications.[44–46] In the first publication, Karrer et al[44] attributed the authorship of this value to Keller. In the other 2 publications, however, it is uncertain whether they obtained new data of their own or whether these values are the same ones published in the first publication. A similar problem occurs in the case of the 3.950 kcal/g value, published by Wiley and Bigelow.[41] Again, it is not clear whether this datum was measured by these authors (no experimental description is provided) or whether it was a value rounded or averaged from previous reports (no bibliographic citation for the datum was provided in the paper). Given these circumstances, it is clear that any statistical analysis using these values will be highly limited. Therefore, this data set is useful only as marginal reference information.

Alternatively, the heat of combustion value for anhydrous maltose can also be estimated by considering the following: the above-mentioned data for crystallized maltose (bibliographic interval, 3.753 ± 0.067 kcal/g); the relative content of crystallized water in crystallized maltose (18 g of water per each 342 g of anhydrous

Table 5 **Heat of combustion values and bibliographic interval for sucrose[a]**

Sucrose: Dickinson (1915),[19] Cox & Pilcher (1970),[22] Fries (1907),[26] Kharasch (1929),[27] Domalski (1972),[29] Berthelot & Vieille (1887),[37] Gibson (1891),[39] Wiley & Bigelow (1898),[41] Armsby & Fries (1918),[42] Richards & Davis (1920),[43] Karrer & Fioroni (1923),[46] Huffman & Ellis (1935),[47] Miller & Payne (1959)[51]
Cane sugar: Atwater & Bryant (1900),[8] Atwater & Snell (1903),[15] Dickinson (1915),[19] Fries (1907),[26] Kharasch (1929),[27] Rubner (1885),[35] Stohmann (1885),[36] Berthelot & Vieille (1887),[37] Gibson (1891),[39] Karrer & Fioroni (1922)[45]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
3.866 ± 0.002 [(I)b] Stohmann (1885)[36]	21		3.908[(XV)]			3.9396 ± 0.0004 Huffman & Ellis (1935)[47]	4	
3.920 ± 0.004[c] Gibson (1891)[39]	61	5	3.91 ± 0.04 Miller & Payne (1959)[51]	6		3.945 ± 0.0005 Richards & Davis (1920)[43]	17	4
3.950 Wiley & Bigelow (1898)[41]			3.94[(IX)]			3.949 Dickinson (1915)[19]	26	2
3.9552 ± 0.0020 [(I)c] Stohmann & Langbein (1892)[40]	4		3.945 Karrer & Fioroni (1923)[46]					
3.9617 ± 0.0008[c] Berthelot & Vieille (1887)[37]	3		3.9453 ± 0.0003 Karrer & Fioroni (1922)[45]	6				
4.001 ± 0.027 Rubner (1885)[35]	2		3.952[(XVI)]					
4.173 [(III)(XIV)c]			3.952[(XVII)]					
			3.9587[(XVIII)]					
			3.959 Atwater & Snell (1903)[15]	20				
			3.959[(XV)]					
			3.96 Atwater & Bryant (1900)[8]					
			3.9878[(XIX)]					
			4.176 [(XX)b]					

Bibliographic interval: 3.949 ± 0.041

[a]Bold values indicate data that were considered outliers after the methods described in the Statistical Analysis section were applied.
[b]On the basis of Iglewicz (2011)[54] and his boxplot criteria, this datum was considered an outlier in the current review.
[c]Domalski (1972)[29] discredited this datum without providing a supporting argument. Nevertheless, it allows one to consider that this datum could be properly classified in precision level L-l.

maltose); the diluent effect; and the heat of hydration of the anhydrous maltose (HH_{malt}, expressed in kcal/g).

To minimize the effect of possible experimental errors on the estimation of the heat of hydration of maltose, the heat of combustion values for both the anhydrous (HC_{anh} = 3.9493 kcal/g of anhydrous maltose[40]) and the hydrated (HC_{hyd} = 3.7218 kcal/g of hydrated maltose[40]) forms of maltose reported in the same paper by Stohmann and Langbein[40] were considered. Equation 6 was used for the estimation:

$$HC_{anh} = HC_{hyd}\left(MH/MA\right) + HH_{malt} \quad \text{(equation 6)}$$

where MH is the mass of the hydrated substance (eg, 360 g; 342 g of anhydrous substance + 18 g of water) and MA is the mass of the anhydrous substance (eg, 342 g), with the MH/MA ratio being an index to correct the so-called diluent effect of the water. Thus, $HH_{malt} \cong 0.03$ kcal/g.

Then, equation 6 may be used twice to calculate the limit values of the estimated bibliographic interval for anhydrous maltose, using the experimental data for the hydrated form of maltose, as shown below:

$$HC_{anh}^{low} = (3.753 - 0.067)\left(360/342\right) + 0.03$$
$$= 3.91 \frac{kcal}{g} \text{ (lowest extreme)}$$
$$\text{(equation 7)}$$

$$HC_{anh}^{high} = (3.753 + 0.067)\left(360/342\right) + 0.03$$
$$= 4.05 \frac{kcal}{g} \text{(highest extreme)}$$
$$\text{(equation 8)}$$

Therefore, the bibliographic interval proposed for anhydrous maltose is as follows: 3.98 ± 0.07 kcal/g, which is shown in parentheses in the corresponding section of Table 2, part B. It is important to note that the experimental values available for anhydrous maltose fall within this interval (see Table 2, part A), which reinforces the validity of the set of considerations used.

For the rest of the carbohydrates (glucose, sucrose, starch, and cellulose), no special considerations were required, which allowed the respective bibliographic intervals to be obtained by following the calculation procedures described previously; such

Table 6 **Heat of combustion values and bibliographic interval for starch[a]**

Starch: Atwater & Bryant (1900),[8] Fries (1907),[26] Kharasch (1929),[27] Huffman & Duncan (1944),[28] Stohmann (1885),[36] Berthelot & Vieille (1887),[37] Gibson (1891),[39] Stohmann & Langbein (1892),[40] Wiley & Bigelow (1898),[41] Armsby & Fries (1918),[42] Karrer et al (1921),[44] Karrer & Fioroni (1922),[45] Karrer & Fioroni (1923),[46] Fraps et al (1940),[50] Miller & Payne (1959),[51] Kabo et al (2013)[53]

Precision level LI			Precision level LII			Precision level LIII		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
4.119 ± 0.011[(I)b] Stohmann (1885)[36]	4		**3.963**[(XXI)c,d]			4.086 ± 0.015[e] Fraps et al (1940)[50]	5	
4.129 ± 0.010[(I)f] Stohmann (1885)[36]	3		4.061[(XXII)d]			4.115[d] Armsby & Fries (1918)[42]	1	
4.1597 ± 0.0096[g] Gibson (1891)[39]	4		4.15[f] Kabo et al (2013)[53]		2			
4.1668 ± 0.0101[d] Gibson (1891)[39]	3		4.176[(XXIII)d]					
4.1736 ± 0.0021[(I)f] Stohmann & Langbein (1892)[40]	3		4.182[(XXIV)d]					
4.1912 ± 0.0047[(I)b] Stohmann & Langbein (1892)[40]	3		4.182[e] Karrer & Fioroni (1922)[45]					
4.200[e] Wiley & Bigelow (1898)[41]			4.182[e] Karrer & Fioroni (1923)[46]					
4.20[e] Atwater & Bryant (1900)[8]			4.1825[(XXV),e]					
4.2281 ± 0.0095[e] Berthelot & Vieille (1887)[37]	4		4.183[(XXVI)e]					
4.479[(III)(XIV)e]			4.19 ± 0.04[e] Miller & Payne (1959)[51]	6				
			4.200[(X)d]					
			4.230[(XII)d]					

Bibliographic interval: 4.163 ± 0.090

[a]Bold values indicate data that were considered outliers after the methods described in the Statistical Analysis section were applied.
[b]Carbohydrate obtained from rice.
[c]On the basis of Iglewicz (2011)[54] and his boxplot criteria, this datum was considered an outlier in the current review.
[d]Carbohydrate obtained from corn.
[e]Carbohydrate obtained from unknown source.
[f]Carbohydrate obtained from potato.
[g]Carbohydrate obtained from arrowroot.

intervals are presented at the end of Tables 4 through 7.

Thus, as a result of the above-described analysis, the following values are proposed here as representatives of the respective heats of combustion (central value of the bibliographic interval, expressed in kcal/g): maltose (Table 2), 3.98; fructose (Table 3), 3.74; glucose (Table 4), 3.73; sucrose (Table 5), 3.95; starch (Table 6), 4.16; and cellulose (Table 7), 4.16. Because the S_w values are roughly 0.03 kcal/g, it was considered appropriate to report the representative values to only 2 places after the decimal point.

The other aim of this paper was to estimate the level of imprecision for the above-mentioned proposed representative values and to establish, for each carbohydrate, intervals within which the actual heat of combustion value would very probably be included. These intervals are very useful when additional calculus may be needed (eg, those calculations required to estimate the total heat produced by the combustion of a particular food) and the overall error involved must be estimated. The following intervals (expressed in kcal/g) are therefore proposed: maltose (Table 2), 3.91 to 4.05; fructose (Table 3), 3.71 to 3.77; glucose (Table 4), 3.69 to 3.78; sucrose (Table 5), 3.91 to 3.99; starch (Table 6), 4.07 to 4.25; and cellulose (Table 7), 4.05 to 4.26. These intervals are the bibliographic intervals, but rounded and reported to only 2 places after the decimal point.

Finally, to provide data about the magnitude of the possible error involved for each type of carbohydrate when the respective representative value is used, the maximum expected error is reported as an index, which is expressed as a percentage of the respective representative value. The estimation of such an index assumes that the actual heat of combustion value falls within the respective bibliographic interval. These indexes are as follows: maltose, 1.8%; fructose, 0.8%; glucose, 1.3%; sucrose, 1.0%; starch, 2.2%; and cellulose, 2.6%.

Table 7 **Heat of combustion values and bibliographic interval for cellulose[a]**

Cellulose: Atwater & Bryant (1900),[8] Fries (1907),[26] Kharasch (1929),[27] Jessup & Prosen (1950),[33] Berthelot & Vieille (1885),[34] Stohmann (1885),[36] Berthelot & Vieille (1887),[37] Stohmann & Langbein (1892),[40] Wiley & Bigelow (1898),[41] Richards & Davis (1920),[43] Karrer & Fioroni (1922),[45] Karrer & Fioroni (1923),[46] Blokhin et al (2011)[52]

Precision level L-I			Precision level L-II			Precision level L-III		
$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m	$\bar{X} \pm se$	n	m
4.146 ± 0.014[(I)] Stohmann (1885)[36]	3		4.020 Richards & Davis (1920)[43]					
4.1859 ± 0.0026[(I)] Stohmann & Langbein (1892)[40]	11	4	4.085 ± 0.047 Blokhin et al (2011)[52]	4	4			
4.200 ± 0.004 Berthelot & Vieille (1885)[34]	2		4.140[(XXVII)]					
4.200 Wiley & Bigelow (1898)[41]			4.140[(XXVIII)]					
4.20 Atwater & Bryant (1900)[8]			4.146 ± 0.002 Jessup & Prosen (1950)[33]	4				
4.45[(XIV)b]			4.154 ± 0.013 Jessup & Prosen (1950)[33]	3				
			4.155[(XXIX)]					
			4.185 Karrer & Fioroni (1922)[45]					
			4.185 Karrer & Fioroni (1923)[46]					
			4.205[(XXX)]					
			4.209[(XXVIII)]					

Bibliographic interval: 4.157 ± 0.103

[a]Bold values indicate data that were considered outliers after the methods described in the Statistical Analysis section were applied.
[b]On the basis of Iglewicz (2011)[54] and his boxplot criteria, this datum was considered an outlier in the current review.

CONCLUSION

This exhaustive bibliographic review identified almost 100 heats of combustion of carbohydrates that were published during the 19th, 20th, and 21st centuries. The data collected were statistically analyzed to propose a representative value (expectedly, the value with the least magnitude of inaccuracy) and a so-called bibliographic interval (an interval containing, very probably, the actual heat of combustion value) for each of the 6 carbohydrates more commonly contained in plant-source foods. These values can be immediately useful; therefore, as a first step to obtain more precise and accurate values for the metabolizable energy applicable to specific food groups that contain important amounts of carbohydrates, the results of this work were used in a parallel study[60] to calculate the total heat of combustion producible in 68 fruits, vegetables, or cereals. Further application of the results presented here may improve the accuracy of nutritional strategies such as dietary intake estimation, diet design, food labeling, functional food design, development of enteral and parenteral formulas, and adjustment of portion sizes, which in turn may enhance the prevention or treatment of degenerative chronic diseases.

Acknowledgments

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