

# Distribution of Tocopherols in Wet- and Dry-Milled Corn Products<sup>1</sup>

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## ABSTRACT

The concentration of tocols and tocotrienols was determined in wet- and dry-milled corn products. Although recovery of dry matter and oil was good by both milling operations, loss of tocopherols was observed. The respective recoveries of alpha-tocol and total tocopherols were 68 and 73% after dry-milling and 18 and 27% after wet-milling. Tocopherols were highly concentrated in the germ products from both dry-milling (196 p.p.m.) and wet-milling (85 p.p.m.). The other corn products, therefore, had a low tocopherol content (grits, 15.4 p.p.m.; flour, 16.7 p.p.m.; and high-fat meal, 26.8 p.p.m.). The difference between total tocopherol concentrations in the germ products from wet- and dry-milling suggested that the manner in which this product was treated contributed significantly to the observed loss of tocopherols.

Products obtained after processing of cereal grains vary widely in concentration of tocopherols (1,2). Herting and Drury (1) showed a high apparent loss of tocopherol in products derived from the endosperm fraction of cereal grains. This loss was attributed to partial destruction of tocopherol during processing and to variation in tocopherol content among cereal fractions.

A high concentration of tocols in the germ and of tocotrienols in the endosperm has been reported for corn (3) and wheat (4). The effect of industrial processing on the tocopherol content of cereals can be estimated only after all the fractions produced by these processes have been analyzed.

An investigation was made to determine the concentration of tocols and

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tocotrienols in the products obtained from wet- and dry-milled corn and to estimate the effect of processing.

### MATERIALS AND METHODS

A sample of CX410 hybrid corn was obtained from Bear Hybrid Corn Co., Inc., Decatur, Ill., 1969 crop. Approximately 1.5 kg. of this hybrid was wet-milled (5) and dry-milled (6) by methods which are comparable to the industrial processes. After a portion of each product was ground to 40 mesh in a Wiley mill, duplicate samples were extracted immediately with ethanol according to the procedures outlined by Quaipe and Harris (7). The corn lipids were saponified and unsaponifiables were isolated by the procedure described by the Analytical Methods Committee, Society for Analytical Chemistry, London (8). The thin-layer chromatographic method of Whittle and Pennock (9) for the isolation and separation of tocols and tocotrienols was used with some modification (3). Recovery of alpha- and gamma-tocol by this procedure was  $83 \pm 1\%$ . The limit of detection of tocopherols by this method is 5% of the total tocopherol concentration in each fraction. Oil content was determined according to the Official Methods of Analysis of the Association of Official Analytical Chemists (10).

### RESULTS AND DISCUSSION

Tocopherol concentrations in wet- and dry-milled corn products are given in Table I. Neither beta- nor delta-tocopherols were observed in any product of this

TABLE I. CONCENTRATION OF TOCOPHEROLS IN WET- AND DRY-MILLED CORN PRODUCTS<sup>a</sup>

| Fraction                   | $\alpha$ -T <sup>b</sup> | $\alpha$ -T-3 <sup>b</sup> | $\gamma$ -T | $\gamma$ -T-3 | Total |
|----------------------------|--------------------------|----------------------------|-------------|---------------|-------|
| Whole                      | 14.3                     | 5.9                        | 29.4        | 10.5          | 60.1  |
| Dry-milled products        |                          |                            |             |               |       |
| Germ                       | 57                       | ... <sup>c</sup>           | 139         | ...           | 196   |
| Low-fat meal               | 0.7                      | 2.8                        | 3.6         | 6.8           | 13.9  |
| High-fat meal              | 2.6                      | 6.4                        | 8.2         | 9.6           | 26.8  |
| Flour                      | 1.3                      | 3.6                        | 3.7         | 7.9           | 16.5  |
| Degermer fines             | 2.2                      | 5.1                        | 6.4         | 9.6           | 23.3  |
| Tailings                   | 4.7                      | 7.4                        | 17.3        | 10.7          | 40.1  |
| Grits                      | 1.3                      | 3.8                        | 4.0         | 6.3           | 15.4  |
| Hull                       | 2.1                      | 2.6                        | 5.8         | 3.5           | 14.0  |
| Wet-milled products        |                          |                            |             |               |       |
| Germ                       | 19                       | ...                        | 66          | ...           | 85    |
| Coarse fiber               | 4.5                      | 5.3                        | 6.4         | 9.2           | 25.4  |
| Fine fiber                 | 2.8                      | 7.6                        | 8.3         | 10.6          | 29.2  |
| Gluten                     | 6.8                      | 16.4                       | 26.1        | 29.2          | 78.5  |
| Starch                     | ...                      | ...                        | ...         | ...           | ...   |
| Steep water <sup>d</sup>   | ...                      | ...                        | ...         | ...           | ...   |
| Process water <sup>d</sup> | ...                      | ...                        | ...         | ...           | ...   |

<sup>a</sup>All data are expressed in  $\gamma$  tocopherol per g. of dry matter.

<sup>b</sup>T = tocol; T-3 = tocotrienol.

<sup>c</sup>An ellipsis signifies that this tocopherol was not observed to be present.

<sup>d</sup>The ether extract of this sample was analyzed for tocopherol content.

TABLE II. TOCOPHEROL AND OIL RECOVERY FROM MILLED CORN PRODUCTS

| Fraction            | Weight of<br>Dry Matter |      | Oil     |            | Tocopherol <sup>a</sup> |                  |       |       | Total |
|---------------------|-------------------------|------|---------|------------|-------------------------|------------------|-------|-------|-------|
|                     | g.                      | %    | %, d.b. | g./100 g.γ | α-T                     | α-T-3            | γ-T   | γ-T-3 |       |
| Dry-milled products |                         |      |         |            |                         |                  |       |       |       |
| Germ                | 230                     | 14.4 | 24.1    | 3.5        | 8.2                     | ... <sup>c</sup> | 20.1  | ...   | 28.3  |
| Low-fat meal        | 132                     | 8.3  | 1.2     | 0.1        | 0.1                     | 0.2              | 0.3   | 0.6   | 1.2   |
| High-fat meal       | 127                     | 8.0  | 2.4     | 0.2        | 0.2                     | 0.5              | 0.7   | 0.8   | 2.2   |
| Flour               | 91                      | 5.7  | 1.8     | 0.1        | 0.1                     | 0.2              | 0.2   | 0.5   | 1.0   |
| Degermer fines      | 30                      | 1.9  | 3.1     | 0.1        | 0.0                     | 0.1              | 0.1   | 0.2   | 0.4   |
| Tailings            | 95                      | 5.9  | 1.2     | 0.1        | 0.3                     | 0.4              | 1.0   | 0.6   | 2.3   |
| Grits               | 764                     | 47.9 | 0.7     | 0.3        | 0.6                     | 1.8              | 1.9   | 3.0   | 7.3   |
| Hull                | 126                     | 7.9  | 1.2     | 0.1        | 0.2                     | 0.2              | 0.5   | 0.3   | 1.2   |
| Total               | 1595                    |      |         | 4.5        | 9.7                     | 3.4              | 24.8  | 6.0   | 43.9  |
|                     | (96.2%) <sup>d</sup>    |      |         | (94%)      | (68%)                   | (58%)            | (84%) | (57%) | (73%) |
| Wet-milled products |                         |      |         |            |                         |                  |       |       |       |
| Germ                | 88                      | 6.6  | 39.5    | 2.6        | 1.3                     | ...              | 4.4   | ...   | 5.7   |
| Coarse fiber        | 137                     | 10.3 | 5.0     | 0.5        | 0.5                     | 0.5              | 0.7   | 0.9   | 2.6   |
| Fine fiber          | 56                      | 4.2  | 4.2     | 0.2        | 0.1                     | 0.3              | 0.3   | 0.4   | 1.1   |
| Gluten              | 119                     | 9.0  | 10.5    | 0.9        | 0.6                     | 1.5              | 2.3   | 2.6   | 7.0   |
| Starch              | 832                     | 62.8 | 0.0     | ...        | ...                     | ...              | ...   | ...   | ...   |
| Steep water         | 51                      | 3.9  | ...     | ...        | ...                     | ...              | ...   | ...   | ...   |
| Process water       | 41                      | 3.1  | ...     | ...        | ...                     | ...              | ...   | ...   | ...   |
| Total               | 1324                    |      |         | 4.2        | 2.5                     | 2.3              | 7.7   | 3.9   | 16.4  |
|                     | (98.8%)                 |      |         | (88%)      | (18%)                   | (39%)            | (26%) | (37%) | (27%) |
| Whole               | ...                     | ...  | 4.8     | 4.8        |                         |                  |       |       |       |

<sup>a</sup>All data are expressed in γ tocopherol per g. of dry whole corn.

<sup>b</sup>Dry whole corn.

<sup>c</sup>An ellipsis signifies negligible contribution.

<sup>d</sup>The figures in parentheses are percentages of recovered material.

corn hybrid. The greatest concentration of tocopherols was found in the germ products (wet-milled, 85 p.p.m.; dry-milled, 196 p.p.m.). No measurable amount of tocotrienols was detected in these germ fractions. This finding is in agreement with previous results on hand-dissected corn fractions (3). The concentration of tocopherols varied in the other dry-milled products from 13.9 p.p.m. in low-fat meal to 40.1 p.p.m. in the tailings. Among the wet-milled products, no tocopherols were detected in starch, steep water, or process water. The highest concentration of tocotrienols occurred in gluten [α-tocotrienol (α-T-3), 16.4 p.p.m.; γ-tocotrienol (γ-T-3), 29.2 p.p.m.].

Recovery of dry matter and oil from both processes was good (Table II). The percentage of dry matter recovered was 96.2 and 98.8% for the dry- and wet-milling process, respectively. Oil recovery was 94% for dry-milling and 88% for wet-milling.

Although oil recovery was good from both milling operations, recovery of tocopherols was low. Tocopherol recovery for each of these milling processes is compared in Table II. Only 18% of the α-tocol (α-T) and 27% of the total tocopherols present in the whole grain were recovered after wet-milling. Recovery

of tocopherol after dry-milling was better. Sixty-eight percent of alpha-tocol and 73% of total tocopherols were recovered from dry-milled corn products.

The effect of processing on germ and nongerm products was estimated from the recovery of tocol and tocotrienol, respectively. Recovery of tocols (79%) from dry-milled germ was greater than the recovery of tocotrienols (57%) from nongerm products. This difference may correlate increased destruction of tocopherols with decreased particle size of the products. The effect of wet-milling appeared to be quite different. Recovery of tocols (23%) after wet-milling was significantly lower than the recovery of tocotrienols (38%), which suggests that the effect of this process on germ is greater than on nongerm products.

The fate of tocopherols during these milling operations has not been investigated, but the low recovery of tocopherols after wet-milling of corn suggests that some chemical transformation of tocopherols has taken place.

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