Received April 21, 1933

Vol. 46 MARCH 1, 1933 No. 5

JOURNAL OF AGRICULTURAL RESEARCH

CONTENTS

ISSUED BY AUTHORITY OF THE SECRETARY OF AGRICULTURE WITH THE COOPERATION OF THE ASSOCIATION OF LAND-GRANT COLLEGES AND UNIVERSITIES

For sale by the Superintendent of Documents, Washington, D. C. - See page 2 of cover for prices

Articles for publication in the Journal must bear the formal approval of the chief of the department bureau or of the director of the experiment station from which the paper emanates. Each manuscript must be accompanied by a statement that it has been read and approved by one or more persons (named) familiar with the subject. The data as represented by tables, graphs, summaries, and conclusions must be approved from the statistical viewpoint by someone (named) competent to judge. All computations should be verified.

Station manuscripts and correspondence concerning them should be addressed to S. W. Fletcher, Director of Research, Pennsylvania Agricultural Experiment Station, State College, Pa.

Published on the first and fifteenth of each month. This volume will consist of twelve numbers and the Contents and Index.

Subscription price:

Entire Journal: Domestic, $2.25 a year (2 volumes)
Foreign, $3.50 a year (2 volumes)
Single numbers: Domestic, 10 cents
Foreign, 15 cents

Articles appearing in the Journal are printed separately and can be obtained by purchase at 5 cents a copy domestic; 8 cents foreign. If separates are desired in quantity, they should be ordered at the time the manuscript is sent to the printer. Address all correspondence regarding subscriptions and purchase of numbers and separates to the Superintendent of Documents, Government Printing Office, Washington, D. C.

JOURNAL OF AGRICULTURAL RESEARCH

VOL. 46 WASHINGTON, D. C., MARCH 1, 1933 No. 5

COMPOSITION OF RHUBARB AT DIFFERENT STAGES OF MATURITY IN RELATION TO ITS USE IN COOKING AND CANNING[1]

By CHARLES W. CULPEPPER,[2] *Physiologist*, and HUBERT H. MOON, *Junior Pomologist, Division of Horticultural Crops and Diseases, Bureau of Plant Industry, United States Department of Agriculture*

REVIEW OF LITERATURE

There is considerable literature dealing with the composition of different portions of the rhubarb plant. Much of this concerns the chemistry of the root and the isolation and identification of the constituents responsible for its therapeutic effects. In the present investigation the composition of the root is of interest because limited quantities of the therapeutically active substances may be present in the petioles and practically all the food constituents of the petiole occur to some extent in the root. The literature on the root is summarized in the standard text books of pharmacology, but particular mention may be made of the work of Tutin and Clewer (*32*),[3] who identified many of the constituents of the root and cleared up much of the confusion in the terminology of this subject. Of special importance also is the work of Müller (*22*), who has isolated certain substances occurring in the root.

Because of the possibility that oxalic acid may occur in quantities large enough to be toxic, considerable work has been done on the nature and amounts of the organic acids of the rhubarb plant and on the toxicity of the oxalic acid as well as that of different parts of the plant itself. The results of these investigations (*1, 2, 3, 6, 10, 16, 19, 21, 23, 24, 27, 28, 31*) show that malic acid predominates in the petiole and that citric acid and oxalic acid occur in much smaller quantities. The total acidity appears to range from 1 to 2 per cent. It is also shown that generally there is not sufficient oxalic acid in the petioles, or leafstalks, to cause harmful effects if they alone are eaten, but most investigators consider it unsafe to eat the leaves when cooked in the same way as spinach or other greens.

From the reports of several investigators (*5, 7, 30*) on the food constituents of rhubarb, it is evident that the food value is rather low and that the constituents vary considerably.

Several investigators have given attention to the ash constituents of rhubarb. From the work of Sherman (*30*) it appears that with the exception of potassium the mineral constituents are low.

The vitamin content of rhubarb has been studied by Pierson and Dutcher (*26*) and by Hessler and Williams (*15*). Their papers are of interest in the present investigation because they deal to some extent with the methods of preparation and preservation.

---

[1] Received for publication May 3, 1932; issued April, 1933.

[2] The material used in this investigation in 1928 was kindly furnished by D. N. Shoemaker, of the Division of Horticultural Crops and Diseases.

[3] Reference is made by number (italic) to Literature Cited, p. 400.

Cruess (*9*) states that rhubarb when canned has an intensely corrosive action upon the tin container and causes swelling and sometimes even perforations. The reports of other investigators (*8*, *17*, *18*, *29*) show a lack of agreement, which may be partly due to differences in the material used.

OBJECT OF THE INVESTIGATION

Investigators have found considerable variation in the composition of rhubarb, in its properties when cooked, and in its behavior when canned. The main object of the present investigation was to determine the effect of age on the composition of rhubarb and the relation of its composition to its suitability for cooking and canning. It was thought advisable to determine also whether seasonal conditions affect its composition. The practical canning and cooking tests were accompanied by a study of the biochemistry of the development of the rhubarb petiole and leaf blade and its relation to seasonal conditions. The results of this phase of the investigation are reported in detail elsewhere (*10*).

SOURCE OF MATERIAL

The material used in the canning and cooking tests in 1926 and 1927 was purchased in the market at Washington, D. C. The appearance of the material indicated that it was all of the same variety, either Victoria or a strain closely resembling it. The material was fresh and at a stage of maturity typical of that generally offered for sale in the markets. The leafstalks were 15 to 18 inches long and weighed 60 to 80 g each.

The material used in 1928 was grown in the test plots at the Arlington Experiment Farm, Rosslyn, Va. The variety was Ruby, a seedling of Victoria (*Rheum hybridum* Murr.), introduced by the Central Experimental Farm, Ottawa, Canada, in 1923 (*20*). This variety was recommended because of the freedom of its leafstalks from stringiness and extreme acidity. The leafstalks are not particularly large but are very numerous and generally contain more than the usual quantity of the red anthocyan pigment in the epidermis. The divisions were obtained from 2-year-old crowns grown in the immediate vicinity of the present planting, which was made in the spring of 1927, the method used being that ordinarily employed in propagating rhubarb. All the chemical analyses reported in this paper were made upon the material grown on the Arlington Experiment Farm in 1928.

SOIL AND CULTURE

The soil on which the rhubarb was grown was a moderately fertile loam to which had been added generous quantities of well-rotted manure. In the fall of 1927 the plants were mulched with barnyard manure, but in 1928 no fertilizer or manure was applied until after the last samples were taken for analysis. The plants were given frequent hoeing throughout the year to remove weeds.

METHODS OF SAMPLING AND ANALYSIS

Four series of samples of known age were secured in the season of 1928. The leaves were just beginning to make their appearance aboveground on April 10. On April 21 the petioles were 2 to 4 inches long and the leaves in many cases had not completely unfolded. On this date a large number of petioles were marked by means of tags, so that leaves of known age could be collected at any time desired. Six collections made at intervals of 7 to 12 days and extending up to June 15 constitute the first series. While this series was being taken the plot was gone over at intervals of 3 to 6 days and the new leaves were tagged as the petioles became 2 to 4 inches long; this treatment was continued to October 9. The leaves tagged in April were considered to be about 10 days old; those tagged in June and July about 5 days old. The higher temperatures of June and July caused more rapid development, so that samples of a given age taken in June or July were at a somewhat later stage of growth than those of like age taken in April or May. From the various lots of tagged leaves, three later series, each consisting of petioles 5 to 60 days old, were collected on June 5, July 6, and October 17, respectively. Broken or injured leaves were always discarded. The leaves were picked by pulling them from the crown, as is customary in harvesting rhubarb. The material for analysis was collected about 10 a. m., and 15 to 25 leaves were used to obtain each chemical sample. Thin cross sections were cut from near the middle of the petioles, and from these petioles 100-g samples were weighed out; enough 95 per cent alcohol was added to bring the concentration up to 75 to 80 per cent. The material was brought to boiling and sealed. For total nitrogen determinations similar samples were dried in a vacuum oven at 70° to 75° C.

The preserved samples were extracted with alcohol and made up to volume. Aliquot portions of these were used for the various determinations. The acid was titrated with N/10 NaOH and calculated as malic acid. The sugars were determined by the volumetric permanganate method recommended by the Association of Official Agricultural Chemists (*4*). The acid-hydrolyzable polysaccharides were determined upon the residue after extraction with alcohol. Total nitrogen was determined by the Kjeldahl method as modified to include nitrate nitrogen. Nitrate nitrogen was determined by the ferrous chloride method as recommended in the Methods of the Association of Official Agricultural Chemists (*4*) for nitrates in meats. The total astringency was determined by the Proctor-Loewenthal method (*25*).

ANALYTICAL RESULTS

The first series differed from the others in that the successive samples making it up were taken at 10-day to 12-day intervals over a period of 55 days, hence under environmental conditions that differed from sample to sample. Later, all the samples constituting a series were taken at one time, and hence had been subjected to identical conditions. Allowing for these differences, the general course of chemical change during development was, broadly speaking, the same in the four series, as is indicated by the similarity of the curves shown in Figures 1 to 6 and by the data given in Table 1.

TABLE 1.—*The composition of rhubarb petioles at different stages of development expressed in percentage of fresh green weight*

Date of sampling	Age	Length of petiole	Total solids	Solids soluble in alcohol	Solids insoluble in alcohol	Total sugars	Acid-hydrolyzable polysaccharides	Acids	Tannins	Nitrate nitrogen	Amino nitrogen	Total nitrogen
	Days	*Inches*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
SERIES A												
April 21	10	2- 4	5. 21	2. 96	2. 25	0. 65	0. 55	0. 999	0. 096	0. 014	0. 045	0. 211
May 5	24	10-12	4. 80	2. 44	2. 36	. 30	. 53	. 948	. 058	. 030	. 029	. 203
May 19	38	12-14	5. 71	2. 80	2. 91	. 42	. 67	. 884	. 086	. 067	. 027	. 178
May 26	45	14-18	5. 87	2. 90	2. 97	. 60	. 68	1. 000	. 109	. 065	. 036	. 155
June 5	55	14-18	5. 81	2. 96	2. 85	. 67	. 58	. 818	. 073	. 077	. 024	. 127
June 15	65	14-18	6. 52	2. 96	3. 56	. 66	. 70	. 749	. 110	. 100	. 020	. 130
SERIES B												
June 5	5	3- 4	5. 33	2. 84	2. 49	0. 40	0. 54	1. 080	0. 122	0. 024	0. 043	0. 198
	8	6-10	4. 83	2. 60	2. 23	. 39	. 48	1. 110	. 109	. 029	. 045	. 160
	11	10-12	4. 60	2. 48	2. 12	. 33	. 46	1. 080	. 127	. 030	. 055	. 136
	15	12-14	4. 84	2. 72	2. 12	. 39	. 47	1. 110	. 096	. 032	. 040	. 142
	19	14-16	4. 56	2. 56	2. 00	. 29	. 42	1. 070	. 088	. 035	. 039	. 149
	25	16-18	5. 25	2. 96	2. 28	. 52	. 45	1. 085	. 091	. 038	. 030	. 127
	32	18-21	5. 81	3. 16	2. 65	. 60	. 58	1. 140	. 087	. 044	. 030	. 134
	40	18-21	6. 17	3. 37	2. 80	. 90	. 72	1. 160	. 079	. 056	. 026	. 130
	55	14-18	5. 81	2. 96	2. 85	. 67	. 58	. 818	. 073	. 077	. 024	. 127
SERIES C												
July 6	5	4-16	6. 57	3. 44	3. 13	0. 40	0. 76	1. 520	0. 168	0. 017	0. 071	0. 267
	9	10-12	6. 45	3. 44	3. 01	. 50	. 79	1. 580	. 153	. 022	. 068	. 228
	13	12-16	6. 15	3. 20	2. 95	. 60	. 77	1. 380	. 123	. 026	. 057	. 197
	28	18-24	7. 19	3. 60	3. 59	1. 05	. 84	1. 320	. 201	. 027	. 043	. 149
	42	20-28	7. 43	3. 48	3. 95	. 91	. 78	1. 150	. 162	. 053	. 038	. 148
	60	20-28	6. 82	3. 96	3. 86	. 56	. 75	. 781	. 265	. 073	. 010	. 121
SERIES D												
October 17	8	9-14	6. 29	3. 56	2. 73	1. 04	0. 63	1. 560	0. 111	0. 023	0. 070	0. 201
	12	14-18	6. 35	3. 44	2. 91	1. 04	. 64	1. 430	. 114	. 026	. 070	. 186
	24	16-20	7. 22	3. 76	3. 46	1. 14	. 74	1. 300	. 110	. 026	. 050	. 180
	40	16-20	7. 23	3. 84	3. 39	1. 05	. 72	1. 280	. 115	. 030	. 041	. 159
	60	16-20	5. 64	2. 52	3. 12	. 58	. 67	. 934	. 100	. 045	. 039	. 132

SOLIDS

Table 1 shows the results of analyses expressed in percentages of the fresh green weight. A high moisture content for all the samples is shown by the low percentages of total solids, although these varied somewhat with the season in which the samples were taken. Early in the season the solids were below 5 per cent in some samples, whereas later in the season they were above 7 per cent in some samples. The curves for the total dry matter in the four series of samples (fig. 1) show that the total solids were generally lower in the series taken in April and June than in the series taken in July and October. The weather records show that the samples taken in April and May grew under conditions of shorter days, and hence with less sunshine and with a lower temperature. The relative intensity of the photosynthetic activity may account for some of the differences in the four series. Since the samples were taken in July and October after several days in which no rain fell it might be assumed that the soil moisture had a considerable effect. These data indicate that a high percentage of solids may be expected in plants grown under conditions of low or medium soil moisture, high temperature, and long hours of sunshine.

The data in Table 1 show also that the percentage of solids varied somewhat with age. Very young petioles, 3 to 4 inches long, had a medium percentage of solids; this decreased during the next few days, then increased, and finally, with one exception, decreased in the very old samples. The petioles seem to have been at about their lowest in solids at the time they were picked for market, or a little earlier.

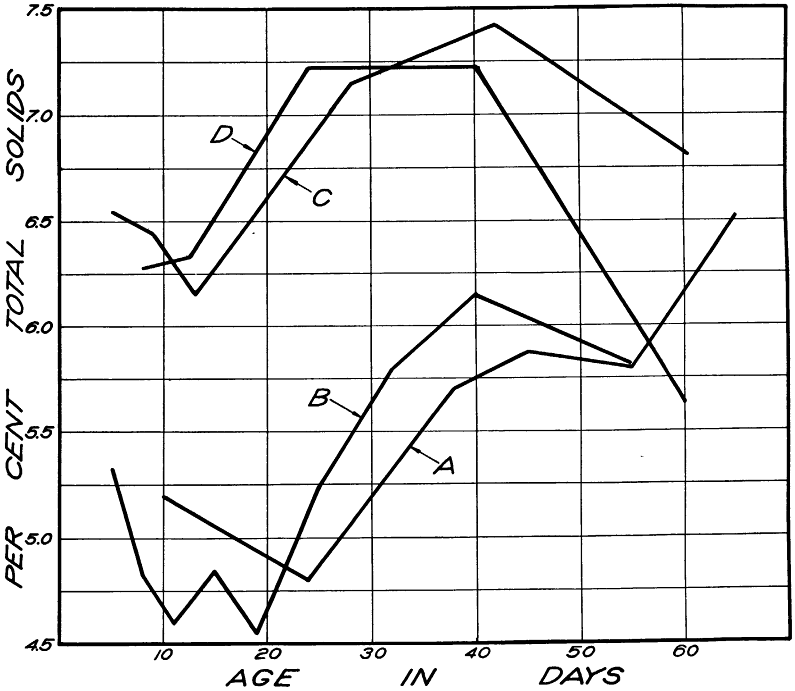

FIGURE 1.—Changes in total solids of rhubarb petioles with increase in age: A, Series collected April 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

About half the total solids were soluble and half insoluble in alcohol. Both soluble and insoluble solids were higher in the series taken in April and May. Insoluble solids varied with age, being lowest in the young samples and highest in the old ones. The soluble solids increased with age or remained nearly constant.

SUGARS

The total sugars were very low and showed no very significant change with age. However, the series taken on July 6 and on October 17 were slightly higher in sugars than those taken earlier. Figure 2 shows the curves for total sugars.

ACID-HYDROLYZABLE POLYSACCHARIDES

The acid-hydrolyzable polysaccharides were also very low. The material in these samples gave a negative iodine test for starch. Differences due to age are not very significant.

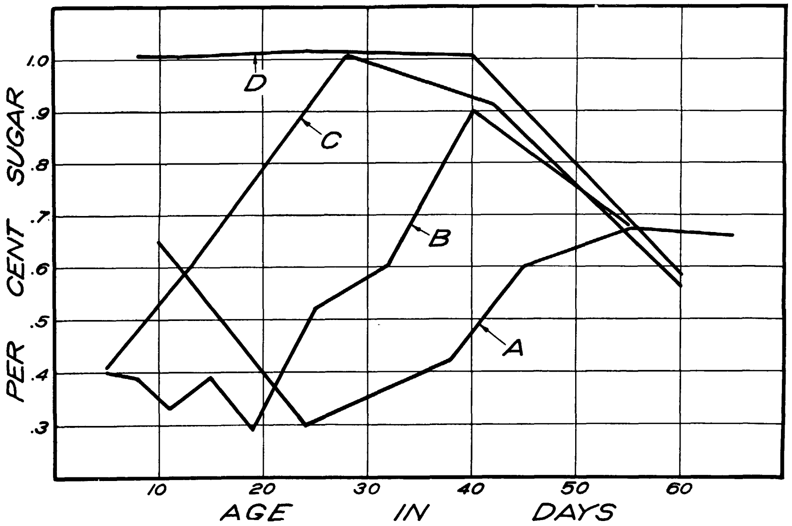

FIGURE 2.—Changes in total sugar content of rhubarb petioles with increase in age: A, Series collected April 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

ACIDS

One of the chief characteristics of rhubarb as a food material is its high acidity. In the variety studied, which is considered comparatively low or medium in acidity, the acid content calculated as malic acid on the fresh green-weight basis may be as high as 1.5 per cent. The high acid content, together with the very low sugar content, makes this variety extremely tart. Except in very old samples, the acidity is considerably higher in the series taken in July and October than in the series taken in April and May. The climatic conditions favorable to high acidity seem to be long hours of intense sunshine, medium or low rainfall, and high temperature. Rhubarb is often said to vary greatly in acidity. In many cases this may be due to varietal differences, but the present study shows that it may also be due to differences in stage of maturity or climatic conditions. The tendency already noted of the titratable acidity to decrease with age is not very noticeable until after the rhubarb has passed the stage in which it is in prime condition for table use. In very old samples the decrease is very marked. It is apparent from Figure 3 that the acidity may remain nearly constant during most of the period in which the material is in prime condition for table use.

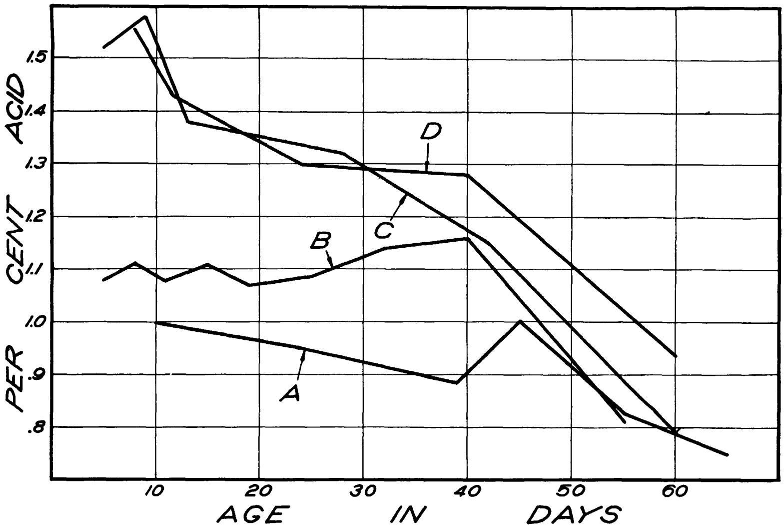

FIGURE 3.—Changes in titratable acidity of rhubarb petioles with increase in age: A, Series collectedApril 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

TOTAL NITROGEN

The total nitrogen in rhubarb is decidedly low, as it is in many fruits. The nitrogen content of the samples analyzed varied from 0.267 to 0.121 per cent. (Table 1.) If these percentages are multiplied by 6.25, the factor used for computing the percentage of protein,

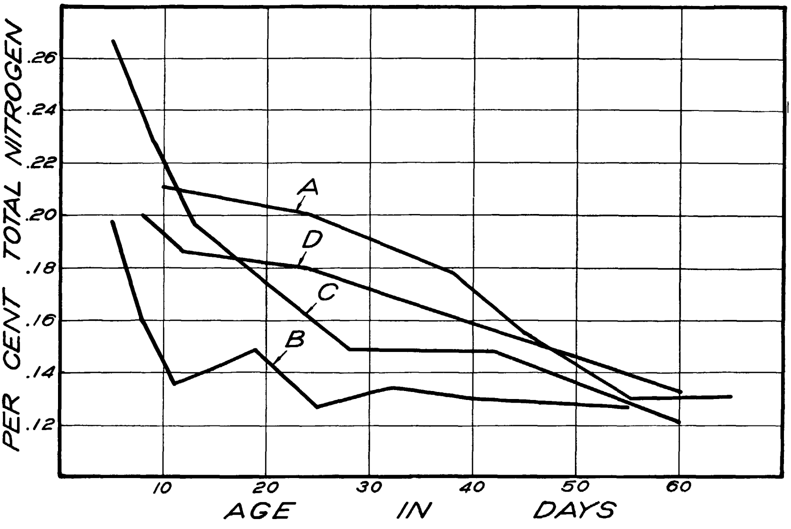

FIGURE 4.—Changes in total nitrogen content of rhubarb petioles with increase in age: A, Series collected April 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

it will be apparent that the protein content of rhubarb is often less than 1 per cent. The total nitrogen, highest in the young samples, decreases rapidly as the petiole develops and more slowly in the older stages. (Fig. 4.)

NITRATE NITROGEN

Changes in the content of nitrate nitrogen are of particular interest. Table 1 shows that in certain cases a high percentage of the total nitrogen is in the form of nitrates. The nitrate nitrogen was lowest in the young samples and increased steadily throughout the life of the leaf. (Fig. 5.) In one sample 77 per cent of the total nitrogen of the old petioles was in the form of nitrates. It may be inferred that the presence of such a high percentage of nitrate is significant as a factor in the corrosion of the metal of the tin container.

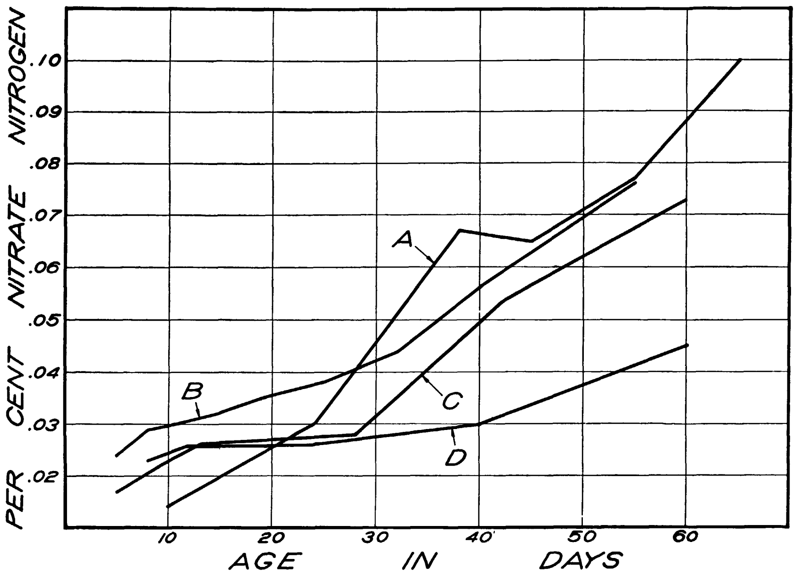

FIGURE 5.—Changes in nitrate nitrogen content of rhubarb petioles with increase in age: A, Series collected April 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

The series of samples taken in October was lower in nitrate nitrogen than those taken earlier. It seems probable that this was due to the reduction of available nitrates in the soil as the season advanced and that the variations in the different series were directly related to variations in the available nitrates in the soil. It would therefore be expected that soil conditions and fertilizer treatment would very materially affect the amount of nitrate nitrogen.

AMINO NITROGEN

In many cases a considerable portion of the total nitrogen is amino nitrogen. It was highest in the young material and decreased as the petiole grew older. Figure 6 shows the results for the four series of samples.

TANNINS

Rhubarb contains a small percentage of astringent substances, or tannins, and it is probable that these are partly responsible for its characteristic flavor. It is not clear just what factors caused the variations of the tannin content of the samples shown in Table 1.

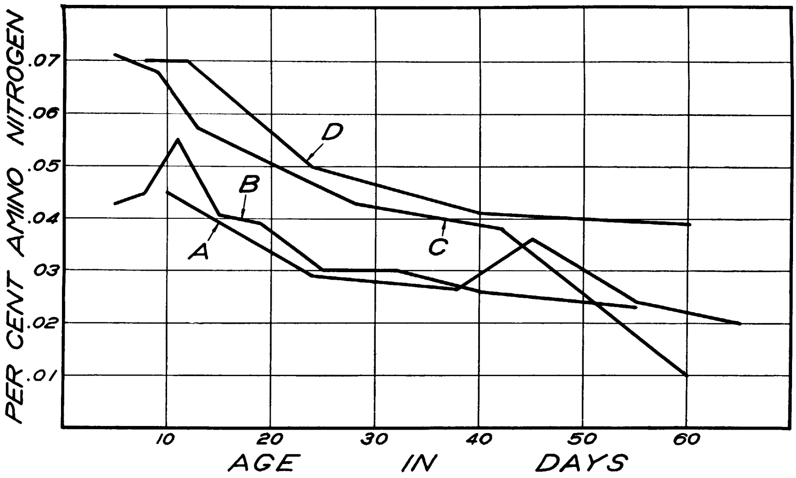

FIGURE 6.—Changes in amino nitrogen content of rhubarb petioles with increase in age: A, Series collected April 21 to June 15; B, series collected June 5; C, series collected July 6; D, series collected October 17

COOKING TESTS

MATERIAL AND METHODS

Rhubarb is commonly used early in the spring, but cooking tests indicate that it may be used at any time throughout the season. In view of the variations in composition as shown by the chemical analyses, some difference in quality from time to time should be expected. The material may be used at any age up to about 30 days when development occurs in the very hottest part of the season, or up to 50 days when development occurs in the cooler part of the season. It becomes somewhat stringy at a much earlier stage in the middle of the summer than in the early spring.

From the standpoint of yield it is not advantageous to harvest when the petioles are only 3 to 4 inches long. The present practice of picking the leaves when the petioles have almost reached their maximum length seems to be about the best procedure. Rhubarb has very nearly maximum moisture content at this stage, yet the difference from earlier stages is not great and may not be very important.

In making the cooking tests some samples were taken in which the petioles were 10 days old and 3 to 4 inches long and, for comparison, other samples were taken that were 10, 18, 30, and 40 days older than the first. The petioles were cut into pieces one-half inch long, placed in a kettle with a small amount of cold water, and allowed to boil for 10 minutes. Then 30 per cent by weight of sugar was added and the material was stirred until the sugar was dissolved. In these tests the very young samples were considered superior to all others. They seemed slightly milder and of better consistency than any of the older ones. There seemed to be very little difference between samples that were taken 18 days and 30 days after the first samples, indicating that the quality remains nearly constant for a considerable time after the petiole ceases its rapid rate of growth. The older samples seemed somewhat more fibrous and less desirable than those taken 18 days after the first samples. The increase in alcohol-insoluble residue shown by the analytical results indicates that the fiber increases; this is in accordance with the cooking tests.

PECTIN CONTENT

When cooked, rhubarb softens and becomes a viscous, semiliquid, colloidal mass. When tested for starch the result was negative. When strained through cheesecloth the liquid gave a voluminous precipitate with alcohol. A precipitate was also formed with calcium hydroxide. When treated with ammonia and then neutralized, an almost insoluble precipitate was formed. When the very young sample was ground and the juice pressed out without heating, a precipitate was formed with alcohol; but the juice of the older petioles gave very little precipitate when so treated. These tests indicate that there is considerable material of the pectin group in the petiole of the rhubarb plant. A large part seems to be protopectin; pectin and pectic acid are probably present also. While pectin was not determined quantitatively, the difference between the precipitates with alcohol indicated that the protopectin decreased greatly as the petiole became older.

ADJUSTMENT OF THE SUGAR-ACID RATIO AND THE CONSISTENCY

The low sugar content and the high acid content of rhubarb make it necessary to add sugar in order to obtain an agreeable taste. The acidity is sometimes so high that the material is improved by soaking in warm water for a short time or in cold water for a long time. For the same reason, partial neutralization is sometimes recommended; a milder product is thus obtained, which will require less sugar to sweeten properly. The acid content, which has been shown to vary considerably with the season, will influence the quantity of sugar that must be added. In these tests, the addition of 30 to 40 per cent of sugar to material having an acid content of 1 per cent made a sauce agreeable to the writers. Of course, individuals vary greatly in their preference as to sweetness. However, the writers concluded that a sugar ratio of about 1:3 is agreeable to most individuals.

Despite the pectin content the moisture content of rhubarb is so high that in making pies it is usually found desirable to add flour or cornstarch to give the material the proper consistency.

CANNING TESTS

In 1926 and 1927 canning tests were made with rhubarb purchased in the market at Washington, D. C. In 1928 the rhubarb used was grown on the Arlington Experiment Farm, as described earlier in this paper. The age of the material in 1926 and 1927 was not known, but it appeared to be in prime condition for table use. In 1928 the rhubarb collected was 20 to 30 days old. The material was brought to the laboratory, trimmed, washed, cut into pieces one-half inch long, and packed in both tin and glass containers as follows:

(1) The pieces were packed tightly in cans or jars, and water was added to fill the interspaces; the containers were then exhausted three minutes in steam at 100° C. and sealed.

(2) The treatment was the same as in 1 except that 60 per cent sirup was added instead of water.

(3) The treatment was the same as in 1 except that no exhaust was given.

(4) The treatment was the same as in 1, except that 60 per cent sirup was added instead of water and no exhaust was given.

(5) The pieces were steamed for five minutes at 100° C. and while hot were pressed tightly into the cans without the addition of either sugar or water.

(6) The treatment was the same as in 5, except that 40 per cent by weight of sugar was added to the hot material and stirred until dissolved.

Some of the rhubarb receiving each treatment was packed in weighed No. 2 cans of three types, namely, plain tin, single-enamel coke-plate, and reenameled charcoal-plate cans. Additional lots of rhubarb receiving treatments 1 and 3 were packed in No. 3 plain tin and single-enamel coke-plate cans. Additional lots receiving treatments 1, 5, and 6 were packed in quart glass jars.

The cans were processed at 100° C. for 15 minutes and then stored for one year. The tin cans were weighed before they were packed with the material and again when they were opened and examined. Large quantities of yellowish crystals or incrustations that had formed in the can during storage frequently adhered tenaciously. This made the method inaccurate for measuring the total amount of corrosion. It was obvious, however, from the differences in the weight of the cans at the beginning and at the end of the test, that unusually large amounts of tin and iron were dissolved from the cans by the material packed in them.

When examined one year after storage the quality of the rhubarb in the glass jars was very nearly equal to that of rhubarb prepared immediately from fresh material.

All the plain tin cans processed without exhaust (treatments 3 and 4) were perceptibly swelled; some were flippers (slightly swelled), and others were swelled tightly as a result of hydrogen formation. The gas had no foul odor and burned violently when ignited, indicating that it was hydrogen. The cans were severely corroded and frequently weighed 0.5 to 1 g less than when the material was placed in them. The tin coating seemed to have been entirely removed from the iron, which appeared dark in color and in many cases was partly covered with adhering crystals or a yellowish incrustation that could not be readily removed by washing. The rhubarb appeared nearly normal, except that it was light brown in color and dull in appearance as compared with that canned in glass, and had a rather disagreeable, metallic taste. It was on the whole an unsatisfactory product. None of the cans were perforated.

The plain tin cans which were sealed hot (treatments 1, 2, 5, and 6) were frequently slightly swelled, but in many cases were entirely normal in appearance. The tin seemed to have been entirely removed from the interior of the can and it appeared almost as severely corroded as the unexhausted cans. None of the cans had become perforated. The contents of the cans, in every way similar to those of the unexhausted cans, were still distinctly acid, having a pH value of 3.52 to 4.0 (0.0001 to 0.0003 N). Since the iron was apparently exposed, the corrosion might be expected to proceed at a rapid rate; however, it was apparent that the action at the end of one year was very much slowed down if not entirely stopped. This was believed to be due to the formation of protective films or incrustations on the surface of the iron. Yellowish coatings, which probably consisted of crystalline or colloidal iron oxalate, were frequently observed.

All the single-enamel cans showed less gas formation than the plain tin cans and were frequently normal in appearance. They were severely corroded and in every can considerable areas of the enamel were so completely loosened that they flaked away when the contents of the can were emptied. From the areas on which the enamel had loosened it appeared that the tin was also completely removed. It seemed that the tin was dissolved away or oxidized underneath the enamel, which promptly fell off when the can was emptied. Frequently large areas of the iron appeared exposed.

The principal difference between the exhausted and nonexhausted enameled cans was in the number of swelled cans. The difference in the intensity of the corrosive action was not very marked.

The reenameled cans were much less corroded than the single-enamel cans. However, they had many small areas from which the enamel and the tin had been removed. There were no tightly swelled cans, and only a few flippers in the unexhausted lots. The material in the reenameled cans was of fair quality but distinctly less pleasing than that canned in glass. It had a slightly bitter taste, probably due to some reaction with the enamel or to the presence of iron or tin salts of the organic acids present.

The cans treated by the addition of a sugar sirup instead of water were slightly less corroded, but the differences were not very pronounced. The yellowish coating previously mentioned was sometimes quite apparent in these lots.

The cans packed without the addition of water (treatments 5 and 6) were similar to those from the corresponding lots with water added. The corrosion was more intense but not as great as would have been expected as a consequence of the larger quantity of material in these cans.

The results differed somewhat in the three years. The material purchased in the market at Washington, D. C., seemed to act upon the cans more severely than did the variety grown on the Arlington Experiment Farm.

The question arises as to what constituents are responsible for this severe corrosive action on the can. The results in general point very definitely to the presence of two constituents: (1) Oxalic acid or its salts, accompanied by high total acidity due chiefly to malic acid, and (2) nitrates.

Clough and Clark (*8*) conclude that corrosion is due to the oxygen content of the porous stems of the rhubarb. Joslyn (*17*) states that the corrosive action is due to the oxygen content and not to the high acidity. From certain tests made by Kohman (*18*), he concludes that the substance responsible "is not oxygen but a substance that behaves like oxygen." De Fouw (*14*) states that nitrates are the only salts that appreciably affect the rate of corrosion of tin by organic acids. Culpepper and Moon (*11*) have shown that the corrosion of tin cans filled with solutions of organic acids is tremendously increased by the presence of nitrates. Under certain conditions the action occurs without the formation of appreciable amounts of gas. Serger (*29*) finds that in canned meats nitrates may cause corrosion of the tin container. Culpepper and Moon (*13*) have shown that oxalic acid is much more corrosive than other organic acids. Although very little free oxalic acid is present in the petioles, it occurs as the acid potassium salt. Whether the potassium salt would corrode the can in a similar manner is not known. Serger (*29*) attributes the corrosive action of rhubarb to its oxalic acid content. In the tests here reported the formation of yellowish crystals and a yellowish coating suggests that iron oxalate is one of the products formed. The content of oxalic acid or its salts in rhubarb petioles has been shown by various workers to vary from 0.1 to 0.7 per cent. Culpepper and Moon (*12*) estimated that there was 6 per cent of air by volume in one sample of rhubarb. The gas content is less than this in the young material and greater than this in the old material. Even in the unexhausted cans this would not be sufficient to account for the amount of corrosion that is apparent.

The analytical results of the present investigation indicate that there is at times as high as 0.1 per cent of nitrate nitrogen in the material. A No. 3 can containing 530 g of rhubarb would contain 0.53 g of nitrate nitrogen, or 3.7 g of potassium nitrate. In cases where there is 0.03 per cent of nitrate nitrogen, which is frequently the case at the stage at which rhubarb is canned, there would be 1.1 g of potassium nitrate. This amount is more than ample to account for the action of the material on the can, especially an acid material like rhubarb. Culpepper and Moon (*13*) found that oxalic acid in a concentration of 0.5 per cent caused swelling in one lot of plain tin cans. Therefore it would be expected that if oxalic acid alone were responsible the cans would become tightly swelled. In the tests of Kohman (*18*) the gas formed was not sufficient to swell the can. In the present tests the cans were seldom swelled. The work of Clough and Clark (*8*) and Kohman (*18*) shows that the substance responsible for the swelling is highly soluble in water, which is true of most salts of nitric acid. The behavior in general indicates that nitrate nitrogen, occurring as a constituent in the material, is an important cause of corrosion in canned rhubarb.

The analytical results have shown that there is considerable variation in the nitrate content of rhubarb at different ages and in different seasons. Since soils under different cultural practices may contain various amounts of nitrate nitrogen and since the amount in the soil affects the amount in the plant, one must conclude that the nitrate content of the material used by different workers is subject to wide variation. Inasmuch as the oxalic acid also varies it seems reasonable to suppose that these variations may account for some of the differences in the results of canning tests by different workers.

SUMMARY

A study has been made of the chemical changes that occur in the petioles of rhubarb with increasing age and changing seasonal conditions. It has been shown that these changes influence the cooking and canning quality of the material.

It was found that the total solids did not vary greatly with age. They were high in the very young petioles, decreased for several days when the petioles were elongating most rapidly, increased slightly during the period of maximum photosynthetic activity, and finally decreased somewhat in the very old material. Marked differences were noted in the samples taken at different seasons. The series

taken in July and October were higher in solids than the series taken in April, May, and June.

The titratable acidity did not vary greatly with age until the petioles were very old, when a marked decrease was noted. There was a very marked difference in the acidity of samples taken at different periods of the season. Acidity was high in the series taken in July and October and low in the series taken in April, May, and June.

Rhubarb is very low in sugars and acid-hydrolyzable polysaccharides and variations in the amounts of these constituents are not particularly significant.

The total nitrogen was highest in the young material and decreased somewhat with age. The amino nitrogen likewise decreased with age. The nitrate nitrogen increased greatly as the age of the material increased. These variations were influenced considerably by seasonal conditions.

Qualitative tests indicate that there are present in the rhubarb petiole pectinlike substances that have considerable influence upon the cooking quality of the material. These substances seem to be largely protopectin.

The low carbohydrate content, the high acid content, and the high moisture content are responsible for many of the characteristics of the material as a food product and explain much of its behavior in cooking.

Rhubarb when packed in plain tin cans had a very severe corrosive action upon the metals of the container. The presence of the resulting metallic compounds had a very pronounced detrimental effect upon the taste and appearance of the material. A high-grade reenameled tin can greatly lessened the amount of corrosion and caused a corresponding improvement in the flavor of the material.

Probably one very important factor in the corrosion is the presence of nitrates. Oxalic acid, accompanied by a high malic acid content, is also thought to be of much importance. The variation due to the age of the material and the seasonal conditions in the amount of nitrates present suggests that differences in the nitrate content may be the cause of the differences in the results obtained by different workers.

The results of the present investigation indicate that rhubarb may be used either for cooking or canning at any time during the growing season if care is taken to select petioles at the proper stage of maturity.

LITERATURE CITED

(1) Anonymous
1917. POISONING BY RHUBARB LEAVES. Lancet [London] 192:847.

(2) Angerhausen, J.
1920. OXALSÄURE IN RHABARBER UND DIE ENTGIFTUNG VON RHABARBERZUBEREITUNGEN. Ztschr. Untersuch. Nahr. u. Genussmtl. 39:81–87.

(3) ———
1920. UBER SAFT AUS RHABARBERSTEILEN. Ztschr. Untersuch. Nahr. u. Genussmtl. 39:122–130.

(4) Association of Official Agricultural Chemists
1925. OFFICIAL AND TENTATIVE METHODS OF ANALYSIS, AS COMPILED BY THE COMMITTEE ON EDITING METHODS OF ANALYSIS, REVISED TO JULY 1, 1924. Ed. 2, 535 p., illus. Washington, D. C.

(5) Bell, M., Long, L. M., and Hill, E.
1925. THE AVAILABLE CARBOHYDRATE CONTENT OF SOME FRUITS AND VEGETABLES. Jour. Metabolic Research 7:195–196.

(6) CASTORO, M.
1902. DARSTELLUNG VON ÄPFELSAÜRE DEN STENGELN DER RHABARBERPFLANZEN. Landw. Vers. Sta. 56:423–426.

(7) CHATFIELD, C., and MCLAUGHLIN, L. I.
1928. PROXIMATE COMPOSITION OF FRESH FRUITS. U. S. Dept. Agr. Circ. 50, 20 p.

(8) CLOUGH, R. W., and CLARK, E. D.
1925. SPRINGERS AND SWELLS IN CANNED RHUBARB. Canning Age 6:490–491.

(9) CRUESS, W. V.
1924. COMMERCIAL FRUIT AND VEGETABLE PRODUCTS; A TEXTBOOK FOR STUDENT, INVESTIGATOR, AND MANUFACTURER. 530 p., illus. New York.

(10) CULPEPPER, C. W., and CALDWELL, J. S.
1932. THE RELATION OF AGE AND SEASONAL CONDITIONS TO THE COMPOSITION OF ROOT, PETIOLE AND LEAF-BLADE IN RHEUM HYBRIDUM. Plant Physiol. 7:447–449.

(11) ——— and MOON, H. H.
1928. THE EFFECT OF NITRATES UPON CORROSION IN TIN CANS. EXPERIMENTATION SUGGESTS THAT THE CORROSION CAUSED BY PUMPKIN IS PARTLY DUE TO NITRATES. Canning Age 9:619–620.

(12) ——— and MOON, H. H.
1929. SPECIFIC GRAVITY DETERMINATIONS AS A GUIDE IN SELECTION OF SUITABLE MATERIAL FOR CANNING AND IN EFFECTIVE CONTROL OF EXHAUST. Canner 68 (8):21–24.

(13) ——— and MOON, H. H.
1929. THE CORROSIVE ACTION OF ORGANIC ACIDS UPON THE TIN CAN. Canner 68 (9):13–16.

(14) FOUW, C. L. DE
1918. INWERKING VAN ORGANISCHE ZUREN OP METALEN. Pharm. Weekbl. 55:1497–1499.

(15) HESSLER, M. C., and WILLIAMS, Z.
1929. THE ANTISCORBUTIC PROPERTY OF APPLE AND RHUBARB. Missouri Agr. Expt. Sta. Bul. 272:68.

(16) ITALLIE, L. VAN, and LEMKES, H. J.
1917. HET OXAALZUURGEHALTE VAN RHABARBER BLADEN EN-STELEN. Pharm. Weekbl. 54:1234–1238.

(17) JOSLYN, M. A.
1929. WOES OF RHUBARB CANNING TOLD. Western Canner and Packer. 21 (6):11–13, illus.

(18) KOHMAN, E. A.
1926. PERFORATION STUDIES. Canning Age 7:187–191.

(19) LEFFMANN, H.
1919. DEATH FROM RHUBARB LEAVES DUE TO OXALIC ACID POISONING. Jour. Amer. Med. Assoc. 73:928–929.

(20) MACOUN, W. T.
1924. REPORT OF THE DOMINION HORTICULTURIST FOR THE YEAR 1923. Canada Cent. Expt. Farms, Div. Hort. Rpt. 1923–24, 54 p., illus.

(21) MAUE, G.
1920. ÜBER DIE INHALTSSTOFFE DER RHABARBERBLÄTTER. Ztschr. Untersuch. Nahr. u. Genussmtl. 40:345–350.

(22) MÜLLER, H.
1911. THE OCCURRENCE OF ALIZARIN IN RHUBARB. Jour. Chem. Soc. [London] Trans. 99:967–968.

(23) NELSON, E. K.
1928. THE ACIDS OF FRUITS. Amer. Med. (n. s. 23) 34:812–815.

(24) ——— and MOTTERN, H. H.
1931. ORGANIC ACIDS OF SPINACH, BROCCOLI AND LETTUCE. Jour. Amer. Chem. Soc. 53:1909–1912.

(25) NEUBAUER, C.
1872. STUDIEN ÜBER DEN ROTHWEIN. Ann. Oenologie 2:1–41, illus.

(26) PIERSON, E. M., and DUTCHER, R. A.
1920. RHUBARB AS AN ANTISCORBUTIC. Science (n. s.) 51:70.

(27) RYDER, A. E.
1930. THE OXALIC ACID CONTENT OF VEGETABLES USED AS GREENS. Jour. Home Econ. 22:309–314.

(28) SCHAFFER, F.
1897. IN DER SCHWEIZ BEOBACHTETE FÄLSCHUNGEN. BERICHT ÜBER DIE UNTERSUCHUNG DER NAHRUNGSMITTEL ETC. WAHREND DES JAHRES 1896 IN KANTON BERN. Chem. Zentbl. 68 (2):908–909.
(29) SERGER, H.
1928. TINPLATE FOR CANS FOR PRESERVED GOODS. Food Manfr. 3:481–482, 512–513.
(30) SHERMAN, H. C.
1914. FOOD PRODUCTS. 594 p., illus. New York.
(31) SIPPY, J. J.
1919. DEATH FROM RHUBARB LEAVES DUE TO OXALIC ACID POISONING. Jour. Amer. Med. Assoc. 73:627–628.
(32) TUTIN, F., and CLEWER, H. W. B.
1911. THE CONSTITUENTS OF RHUBARB. Jour. Chem. Soc. [London] Trans. 99:946–967.