

este and 5 g. of thio-urea were added and the mixture heated for 4 hours at 105°. The condensation product insoluble in the alcoholic solution was collected on a filter, then dissolved in water. On acidifying the solution with hydrochloric acid, a copious white amorphous precipitate formed at once. It was somewhat soluble in hot water and slightly more soluble in hot alcohol but could not be obtained from either solvent in crystalline form. The yield was 7 g. or 76%.

Subs., 0.2, 0.2: NH_3 , 22.76, 22.65 cc. 0.1 *N*. Calc. for $\text{C}_3\text{H}_6\text{O}_2\text{N}_2\text{S}$: N, 16.47. Found: N, 15.93, 15.85.

Subs., 0.2: BaSO_4 , 0.2808. Calc.: S, 18.80. Found: 19.28.

Summary.

1. Cyclopropane-1,1-dicarboxylic ester condenses with urea, guanidine and thio-urea to form stable, amorphous products. From comparison with the corresponding cyclobutane and cyclohexane derivatives it is apparent that these products are polymers.

2. Hydrolysis of the urea polymer, followed by elimination of carbon dioxide, gave a crystalline acid with melting point 152° and molecular weight 176 (by titration). Of the acids, $\text{C}_8\text{H}_{12}\text{O}_4$, theoretically possible from hydrolysis of a dimer only the hexahydrophthalic acids are known. It is probable that a cyclopropane-1.5-*spiro*-barbituric acid first formed undergoes rearrangement to vinyl-barbituric acid which then polymerizes. The product would then be a cyclobutane-dibarbituric acid, which on hydrolysis and loss of 2 molecules of carbon dioxide would yield cyclobutane-1,2- or -1,3-di-acetic acid, both of which could exist in *cis* and *trans* forms. It is probable that the polymer is not a *spiro* derivative but rather cyclobutane-dibarbituric acid.

DETROIT, MICHIGAN.

[CONTRIBUTION FROM THE BUREAU OF PLANT CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

CHANGES IN THE COMPOSITION OF PAPRIKAS DURING THE GROWING PERIOD.

BY A. F. SIEVERS AND J. D. McINTYRE.

Received June 9, 1921.

The change in chemical composition of plants during their growth and development has always been an inviting field of research for the chemist and plant physiologist. Especially is this true in connection with fruits, vegetables and drugs. Much work has been done in this direction, particularly when some definite chemical compound is of predominating influence in determining the quality of the product. As examples, one might mention the development of sugars in the orange, sugar-beet, sweet-corn and sweet potato : citric acid in the lemon; volatile

cils in aromatic herbs; and alkaloids or other active principles in medicinal plants. Such studies are of more than mere scientific interest in that they frequently serve to show at what stage of growth a product should be harvested in order to assure maximum quality and the extent to which lack of care in gathering may affect the general quality of the harvest.

The red peppers, which are widely used as condiments, depend to a varying degree on their pungency as a measure of quality. The investigation here recorded was undertaken for the purpose of tracing the development of the pungent principle and sugar in the paprika, a large fruited variety of *Capsicum annuum*, L. The literature records a great deal of work on the composition of paprikas but the investigations appear to deal mostly with the composition of the several parts of the fruit and the effect of additions of foreign matter on such composition. No systematic study of the fruit from its early formation to its maturity appears to have been recorded.

The paprikas were grown at Arlington, Virginia, and at several intervals of the growing season samples of 6 different sizes of fruit were picked. Since a single plant will bear fruit of all stages of development at one time, the above method appeared to be the most feasible means of securing representative samples of fruit of the several stages. The smallest specimens picked included fruit under 25 mm. in length, while the largest specimens were 100 mm. or more in length. Table I shows the average size and weight of the several samples collected.

TABLE I.

AVERAGE SIZE AND WEIGHT OF PAPRIKAS AT SIX STAGES OF GROWTH.

Stage.	Length. Mm.	Diameter. Mm.	Weight. G.	Color.
1	less than 25	7.3	1.89	green
2	25 to 37	10.2	3.10	green
3	37 to 50	14.1	7.77	green
4	50 to 75	18.5 ^a	10.77	a few were slightly red
5	75 to 100	17.6	14.86 ^b	about one-half were red
6	more than 100	all dark red

^a At this stage the maximum diameter was attained. Upon further development the fruit began to shrink or shrivel somewhat; hence, diameter measurements of the last sample were not taken.

^b The maximum weight is reached at this stage. The fruit loses considerably in weight as it matures.

The fruit was carefully freed from adhering soil, and after the stems and calyxes had been removed was spread out thinly to dry in a well ventilated room. The dry pods, consisting of shells, placenta and seeds were then ground and passed through a 40-mesh sieve. The samples were analyzed for moisture, ash, alcohol extract, volatile and non-volatile ether extract and reducing and total sugars. The analyses were made according to the Official and Provisional Methods of Analysis, Bureau of Chemistry *Bulletin* 107 (revised), except in the case of the sugars which were extracted accord-

ing to a modified method and then determined by the official gravimetric method. A summary of the results of the analyses is shown in Table II.

TABLE II.

RESULTS OF THE ANALYSES OF PAPRIKAS AT SIX STAGES OF GROWTH.

Stage.	Moisture. %.	Ash. %.	Ether extract.		Total. %.	Alcohol extract. %.	Sugars.	
			Volatile. %.	Non-volatile. %			Reducing. %.	Total. %.
1	8.46	8.13	0.19	1.95	2.14	18.72	5.81	11.90
2	6.79	7.72	0.17	2.47	2.64	17.03	5.81	13.81
3	7.63	7.57	0.22	4.82	5.04	18.25	6.27	14.72
4	7.19	7.00	0.27	5.24	5.51	19.15	5.90	13.92
5	7.21	6.85	0.24	6.35	6.59	19.24	6.42	13.32
6	7.16	6.78	0.85	8.50	9.18	21.15	8.59	14.39

It will be noted that the ash and ether extract show a definite change through the several stages. The former decreased from 8.13 to 6.78%. The ash was practically all soluble, only slight traces of insoluble matter being present. The total ether extract increased from 2.14 to 9.18% which is a very good indication of the development of the pungent principle. The volatile ether extract, which represents the volatile oil, increased from 0.19 to 0.85%, practically all the increase taking place during the end of the growing period. The alcohol extract shows no definite or decided change and the same may be said about the sugars. The percentage of both total and reducing sugars in the small immature paprikas is exceedingly high as compared with the amount present in the ripe fruit. There are considerable fluctuations in the sugar content during the several stages, due in some measure, possibly, to the tendency of sugars to undergo changes during the drying of the material. The outstanding fact to be noted from these analyses is the increase in the pungency as indicated by the ether extract.

As a rapid means of roughly determining the relative pungency of paprikas, it has been proposed to triturate a definite weighed quantity of the ground pepper in a mortar with sugar, the latter being added a little at a time until a small quantity of the mixture when placed on the tongue does not produce a distinctly pungent taste. This method is, of course, of no analytical value, but when applied to the above 6 samples of paprikas it gave a fair indication of the increase in pungency as the fruit matured. Thus, the quantity of sugar required to mask the pungency of 0.2 g. of the paprika from the first to the last stage was as follows: 0.39, 5.55, 5.52, 7.6, 12.48 and 32.2 g.

In conclusion it may be said that the ether extract is a fairly accurate measure of the maturity of the paprikas, but it is necessary that the normal ether extract of an average sample of such peppers be known for comparison. On the other hand, neither the sugar content nor the alcohol extract changes sufficiently or with such marked regularity as to indicate

the stage at which the fruit was picked. Furthermore, it is evident that even in cases where color is of no consequence and pungency is of first consideration, fully matured fruit must be used to obtain the maximum value.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

DERIVATIVES OF ANTHRAQUINONE. ALIPHATIC THIO-ETHERS, DITHIO-ETHERS, AND THIO-ETHER SULFONIC ACIDS.

By E. EMMET REID, COLIN M. MACKALL AND GEORGE E. MILLER.¹

Received June 10, 1921.

Introduction.

The original object in taking up the study of anthraquinone sulfonic acids was to obtain derivatives which could be used for their ready separation and identification. This object was only partially attained but the reaction tried proved interesting and the products obtained appeared worthy of study, so the investigation was shifted from its original purpose and extended in other directions.

On account of the instability of the esters of sulfonic acids the methods used for the identification of carboxy acids² were not promising and our efforts were directed to the replacement of the sulfonic groups.

It was known that the sulfonic acid group of α -anthraquinone sulfonic acids can be replaced by methoxy³ or phenoxy⁴ groups, and that the resulting compounds $C_{14}H_7O_2.OCH_3$ and $C_{14}H_7O_2.OC_6H_5$ are crystalline and have definite, though rather high melting points. Hence it was thought that a compound of the type $C_{14}H_7O_2.SR$ would be of service. *N*-butyl mercaptan was used as being readily available, and it was thought probable that the compound $C_{14}H_7O_2.SC_4H_9$ would have a low melting point, since sulfur compounds usually melt lower than the corresponding oxygen compounds, and since butyl derivatives are apt to melt considerably lower than methyl, and much lower than phenyl. The desired reaction was found to take place readily, although not quantitatively, when the sulfonic acid group is in the α -position. The resulting compounds were found to have convenient melting points suitable for the identification of anthra-

¹ The work on the 1,5-compounds is from the Doctor's dissertation (1920) of Colin M. Mackall and that on the 1,8-compounds from that of George E. Miller (1920); the α -derivatives were prepared by the other author with some assistance from W. S. Hoffman of this Laboratory and A. T. Frascati in the Laboratory of E. I. du Pont de Nemours and Company.

² THIS JOURNAL, 39, 124, 304, 701, 1727 (1917); 41, 75 (1919); 42, 1043 (1920); and 43, 629 (1921).

³ Bayer and Co., Ger. pat. 156,762.

⁴ Bayer and Co., Ger. pat. 158,531.