

Effect of Ethrel (2-Chloroethyl Phosphonic Acid) on Ripening of Bananas*

by
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The ability of ethylene to stimulate fruits to ripen has been reported in fruits and vegetables (Burg, 1962 and 1965; Hansen, 1966; Burg and Burg, 1968; Dilley, 1969 and Pratt and Goeschl, 1969). Recently, the newly developed compound Ethrel (2-chloroethyl phosphonic acid) which degrades itself to yield ethylene, has been found to be effective in causing ripening of fruits (Russo *et al.* 1968; Iwahoris *et al.* 1969; Robinowitch *et al.* 1970 and Srinivasan *et al.* 1971). The banana variety Robusta, a clone of Dwarf Cavendish group is characterised by the production of heavy bunches with large sized fingers. Despite these attractive features its commercial preference is greatly influenced due to poor development of peel colour, besides prolonged period of ripening. Therefore it was of interest to study the effect of Ethrel on the development of peel colour and ripening in the case of Robusta banana.

Materials and Methods: "Full three quarters" bunches of Robusta banana grown in the College Orchard were selected for the studies. From the bunches so selected, the first three largest hands were employed for the investigation due to the similarity of maturity of the hands.

Ethrel (ACP 68 - 250) a Amchem product has been used for treatments. The treatments comprised aqueous preparation of Ethrel at A: 100, B: 200, C: 500, D: 1000, E: 2000, F: 5000 and G: 5000 ppm dip and H: Smoking the fruits, I: covering the fruits with gunny and J: untreated control. Fifty fruits were considered in each treatment. For treatments A to F, the fruits were kept in an air tight chamber of 60 × 60 × 75 cm dimensions, at room temperature (25°C). A beaker containing 200 ml of aqueous preparation of each of the concentrations was kept at the centre of the chamber amidst the fruits and 5 g of sodium hydroxide pellets were dropped into each beaker in the respective chambers, before closing. An additional treatment G comprised of the dipping of fruits at 5000 ppm Ethrel with 1 per cent Teepol as Wetter. The fruits in treatments G to J were also kept in similar chambers.

The comparative effectiveness of the treatments on the time taken for the ontogeny and completion of ripening of the fruits were reckoned in terms of texture and colour development of peel with reference to Horticultural Colour Chart (Robert, 1938). The initial weight of fruits before treatment and the final

* Awarded Ramasastrulu Munagala Prize - 1971.

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weight of the fruits after complete ripening were recorded and the differences between these were expressed as per cent of loss in weight due to ripening.

Changes in the contents of chlorophyll of banana peel was estimated by extinction of light at 642.5 m μ and 660 m μ in spectronic 20 (Smith and Beintez, 1955) from the fruits sampled before treatment, 24 hours after treatment and on completion of ripening.

Pulp homogenate from the completely ripened fruits in each of the treatments was utilized for determining the following chemical constituents. 1) Total soluble solids was recorded using a hand refractometer and expressed as per cent. 2) Titratable acidity was determined by titrating against decinormal potassium hydroxide using phenolphthalein as an indicator and expressed as per cent of anhydrous citric acid. 3) Total and reducing sugars were estimated colorimetrically as described by Somogyi (1952), while the non-reducing sugars were recorded by difference between these two. 4) Estimation of starch content in 5 g of fruit homogenate was carried out colorimetrically as per the method of Nielson (1943). 5) Total protein content was estimated as per the procedure of Osborne (1962) and 6) the apparent ascorbic acid content was determined by visual titration method using 2, 6-dichlorophenol indophenol (Freed, 1966).

Results: I. *General effect of treatments on ripening and associated constituents:* The Ethrel treatments invariably altered the time taken for complete ripening, peel colour and carbohydrates markedly in comparison with the fruits in control, covered with gunny and smoked. The details in respect to the individual treatment are presented in Fig. 1 and Tables 1 and 2.

TABLE 1. *Effect of Ethrel on degreening of robusta banana*

Treatments	Total chlorophyll content (mg/g of fresh weight)		Colour development in fully ripened fruits
	24 hours after treatment	After complete ripening	
Control	0.5496	0.5333	Agatha green 60
Gunny	0.5021	0.5276	Agatha green 60/1
Smoking	0.4843	0.4458	Pea green 61/1
Ethrel 100 ppm + NaOH	0.5420	0.4778	Pea green 61/1 with yellow patches
200 ppm + NaOH	0.3746	0.3654	-do-
500 ppm + NaOH	0.2919	0.2412	-do-
1000 ppm + NaOH	0.2824	0.1028	Dresden Yellow 64/3
2000 ppm + NaOH	0.2306	0.0718	Empire yellow 603/1
5000 ppm + NaOH	0.1034	0.0461	Empire yellow 603/1
5000 ppm Dip	0.1552	0.0549	Empire yellow 603/1

N. B. Total chlorophyll content before treatment : 0.6552 on an average.

TABLE 2. Effect of Ethrel on the composition of Robusta banana

Treatment	Per cent loss in weight	Total soluble solids per cent	Titrable acidity per cent anhydrous citric acid	Carbohydrates (%)				Protein per cent	Ascorbic acid mg/100 g
				Starch	Total sugar	Reducing sugars	Non reducing sugars		
Control	7.40	15.2	0.45	4.10	11.11	7.69	3.42	1.4	5.80
Smoking	15.50	16.4	0.45	4.50	12.80	8.33	4.47	1.1	5.20
Gunny	11.50	16.8	0.45	4.65	11.62	7.81	3.81	1.2	5.00
Ethrel 100 ppm + NaOH	12.30	16.4	0.45	3.60	13.89	7.41	5.48	1.3	5.30
200 ppm + NaOH	11.70	16.6	0.32	3.05	14.08	8.72	5.31	1.3	4.04
500 ppm + NaOH	15.60	18.0	0.32	2.75	14.29	8.92	5.37	1.4	5.10
1000 ppm + NaOH	16.66	19.0	0.32	1.80	14.70	9.26	5.44	1.4	4.80
2000 ppm + NaOH	16.73	22.0	0.26	0.90	14.28	10.00	4.28	1.5	5.90
5000 ppm + NaOH	17.10	23.0	0.26	0.55	15.63	12.87	2.76	1.5	5.90
5000 ppm Dip	16.83	22.8	0.19	0.45	16.39	12.64	3.75	1.5	4.95

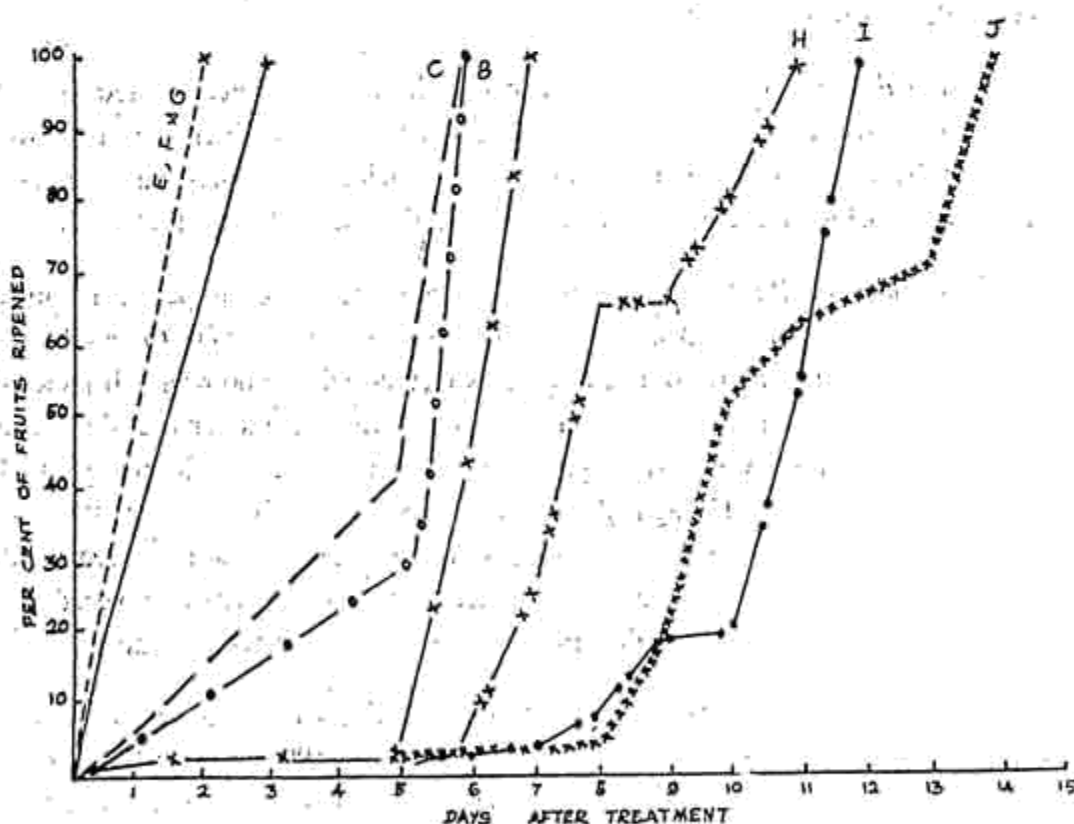


FIG. 1. EFFECT OF ETHREL ON RIPENING OF BANANA VAR. ROBUSTA

Duration of ripening: A pronounced hastening of ripening ranging from 2 to 5 days was brought out by the Ethrel treatments. The effect of Ethrel on

ripening is proportional to its concentration. Fruits treated with Ethrel at 2000 and 5000 ppm with NaOH and those fruits dipped in 5000 ppm of Ethrel with 1 per cent Teepol ripen the fruits completely as early as two days. Whereas 1000, 500, 200 and 100 ppm with NaOH caused the ripening in 4-5 days. On the contrary, ripening of fruits was extended to 11 to 12 days in the case of treatments circulated with smoke and those covered with gunny. Completion of ripening in untreated fruits was noted after a period of 14 days (Fig. 1).

Morphological changes: Most obvious morphological change during ripening was the development of peel colour. While the control fruits and those covered with gunny developed pale green colour, higher concentration of Ethrel, particularly 5000 ppm caused an attractive Dresden Yellow colour. In addition, low concentration of Ethrel at 100, 200 and 500 ppm, admixture of green and yellow colour was observed. Fruits covered with gunny and in control developed Agatha Green, whereas the fruits circulated with smoke developed an unpleasant black peel with Pea Green colour patches (Table 1). The percentage of loss in the weight of the Ethrel treated fruits after complete ripening was estimated to be more than double that of the control. Smoked fruits also showed a considerable loss in weight similar to Ethrel treated fruits (Table 2).

Chemical changes: Ethrel treatments induced an accelerated loss of chlorophyll, starch and titratable acidity and a comparable increase in the total soluble solids, total and reducing sugar contents, while such marked changes in protein and ascorbic acid contents were not brought out by Ethrel treatments.

Total chlorophyll: A rapid and significant decrease in peel chlorophyll content was observed in the Ethrel treatments ranging from 1000 to 5000 ppm, the reduction being more pronounced in fruits treated with 5000 ppm with sodium hydroxide and 5000 ppm with 1 per cent Teepol as dip. Moreover the diminution in chlorophyll content was strikingly proportional to every increase in the concentration of Ethrel. Though degradation was also observed at 100, 200, 500 ppm Ethrel treatments, it was not to such a degree as in 5000 ppm treatments. The peel chlorophyll contents relating to control, smoked and fruits covered with gunny, were eight to ten times higher than the Ethrel treated fruits (Table 1).

Carbohydrate content: A considerable depletion of starch was noticed in Ethrel at 1000 to 5000 ppm with sodium hydroxide and 5000 ppm with 1 per cent Teepol as dip, the reduction being more marked in 5000 ppm Ethrel treatments. In contrast, the starch content in the fruits treated with Ethrel at 100 to 500 ppm was not reduced to such an extent, though comparatively less than control and smoked fruits.

Total and reducing sugars increased predominantly in Ethrel-treated fruits, the increase being in direct proportion with the increase in the concentration of

Ethrel. As such the fruits treated with 5000 ppm of Ethrel contained a higher quantity of total and reducing sugars. However, there were no comparable changes in the non-reducing sugars content due to Ethrel treatments.

Total soluble solids: Total soluble solids recorded an increase in the Ethrel treated fruits for every increase in the concentration of Ethrel. A 50 per cent increase in total soluble solids was registered at 5000 ppm Ethrel treatments than control.

Titrateable acidity: Practically there was no change in the titrateable acidity of the fruits treated with 100 ppm Ethrel, those circulated with smoke and covered with gunny and the fruits in control, while there was a marked reduction in acidity due to Ethrel at 5000 ppm, when given as dip.

Protein content: An increase in protein content was brought out by Ethrel treatments, but it was not marked. In the case of fruits circulated with smoke, there was however a reduction in Protein content (Table 2).

Ascorbic acid content: It was not in any way affected much by all treatments, though little differences existed. In general, the Ethrel treated fruits were better flavoured, while a smoky 'cooked' flavour was felt in the fruits ripened by circulating the smoke.

II. *Effect of Ethrel at 5000 ppm with sodium hydroxide on the stages of ripening of bananas:* In general Ethrel at 5000 ppm with NaOH and as dip showed a distinct influence on the hastening of ripening resulting in the rapid degradation of chlorophyll, starch and titrateable acidity and an increase in simple sugars to a comparatively higher degree. Hence it was of interest to study the changes in these constituents during the different stages of ripening of banana fruits.

TABLE 3. Changes in the constituents of Robusta banana fruit during ripening due to Ethrel at 5000 ppm with sodium hydroxide

Stages of ripening Hours after treatment	Total soluble solids %	Percentage of titrateable acidity (as anhydrous citric acid)	Carbohydrates (%)				Protein per cent	Total chlorophyll content in Banana peel (mg/g fresh wt.)
			Starch	Total sugar	Reducing sugar	Non-reduc- ing sugar		
Before reatment	5.0	0.56	16.50	6.25	3.15	3.10	1.3	0.58
12	8.6	0.45	14.00	8.15	4.25	4.90	1.3	0.50
18	19.0	0.32	3.60	11.25	7.15	4.10	1.4	0.37
24	20.0	0.26	1.80	11.25	8.85	2.40	1.4	0.26
36	21.0	0.19	1.50	12.50	9.50	3.00	1.5	0.12
42	22.0	0.19	0.80	15.25	11.25	4.00	1.5	0.08
48	22.6	0.19	0.40	16.00	11.75	4.25	1.5	0.04

The data on the sequence of changes in respect of 12, 18, 24, 36, 42 and 48 hours after Ethrel treatments, is presented in Table 3. An abrupt increase in total soluble solids per cent, total and reducing sugars and a reduction in starch was evidenced, 12 to 18 hours after treatment and a slight increase thereafter, while the non-reducing sugars increased initially and declined from 18 to 24 hours after treatment followed by a rise from 36 hours onwards. Total chlorophyll content decreased steadily while the acidity reached a minimum 36 hours after treatment.

Discussion: Ripening in banana is associated with degradation of chlorophyll and conversion of starch (Von Loesecke, 1950 and Simmonds, 1959). Fully ripened Robusta banana is pale green in colour due to little loss of chlorophyll and moderate depletion of starch and normally ripening prolongs for a period of 14 days. In the present study, treatment with Ethrel, especially with 5000 ppm, hastened the ripening considerably, resulting in an accelerated degradation of chlorophyll followed by the development of yellow peel. Ethrel also depleted the starch content followed by predominant accumulation of reducing sugars. Such degreening in banana due to Ethrel treatments has been reported by Russo *et al.* (1968). Moreover, the development of yellow peel might also be due to the synthesis of yellow pigments to a little extent, by Ethrel treatments, as reported in other fruits such as tomato and persimmon (Byers *et al.* 1969 and Srinivasan, *et al.* 1971).

In normal ripening of fruits, it is a common experience that ethylene causes immediate ripening of all except very early picked fruits. Further for satisfactory ripening of fruits a minimum threshold level of ethylene in the tissues has been stressed (Burg, 1965). In the absence of applied ethylene the fruits own ethylene appears to play a part although it may exist in low concentration before the commencement of ripening (Brady *et al.* 1970). The considerable hastening of ripening due to the Ethrel treatments, as observed in this study, lend to support to the view that supplementing of exogenous ethylene might have increased the minimum endogenous threshold level. Such stimulation of ripening and associated changes are directly proportional to the concentration of Ethrel.

Further, Ethrel degrades to yield ethylene not only in the presence of plant tissues but also in the presence of added base. As such, when the fruits were dipped in aqueous Ethrel solution, as in the case of dipping fruits in Ethrel 5000 ppm with 1 per cent Teepol, the Ethrel is taken up into the fruit tissues as any other aliphatic acid and subsequently breakdown by cytoplasmic pH with the formation of ethylene (Warner and Leopold, 1969). This finding has been taken advantage of by the earlier investigators (Robinowitch *et al.* 1970 and Srinivasan *et al.* 1971). But this is the first study wherein sodium

hydroxide has been utilised to enhance the pH of Ethrel to evolve ethylene and the exposure of banana fruits to that, hasten the ripening as early as 2 days compared to 14 days in control.

Moreover, there is no much difference between the fruits dipped in 5000 ppm Ethrel and those exposed to Ethrel 5000 ppm added with sodium hydroxide, in regard to the hastening of ripening and associated changes. But, in the case of fruits dipped in Ethrel, the residual degraded products of Ethrel in the tissues may be toxic to the consumers. Such effect, if any, could be avoided by merely exposing the fruits to alkaline Ethrel solution. Moreover this method lend scope for treating large number of bunches by keeping the aqueous preparation of Ethrel with sodium hydroxide or any base at various places of the fruit godowns. While the dipping not only take longer time but also irritate the hands who dip the fruits. However, the exact concentration of Ethrel, the quantity of aqueous solution and sodium hydroxide to ripen a specific number of fruits remain to be studied.

A marked stimulation of ripening and development of yellow peel colour with better flavour in Robusta banana due to Ethrel, offer a promising possibility of enhancing its market value. The present study also has thrown some clues on the ripening mechanism of Robusta banana and in view of the major role of ethylene in hastening ripening, the problem of its biogenesis and exact mechanism of action, need considerable attention and critical study.

Summary: Fifty 'Full three quarters' fruits of Robusta banana were exposed to aqueous solutions of Ethrel (2-chloroethyl phosphonic acid) at 100, 200, 500, 1000, 2000 and 5000 ppm. The fruits were kept inside a chamber at the room temperature (25°C). A beaker containing 200 ml of each of the concentration of Ethrel was kept amidst the fruits and 5 g of sodium hydroxide was dropped into each beaker. An additional treatment comprised of dipping the fruits in Ethrel at 5000 ppm and one per cent Teepol as wetter. Fruits were also covered with gunny and circulated with smoke. Fruits devoid of any treatment served as control.

Ethrel, in general, hastened the ripening in Robusta Banana fruits, the stimulation being marked at 5000 ppm with sodium hydroxide or as dip. The fruits ripened within 2 to 5 days by Ethrel compared to the fruits circulated with smoke, covered with gunny and control where it extended upto 11, 12 and 14 days respectively. A considerable degradation of chlorophyll and a rapid depletion of starch were observed. Ethrel treated fruits also contained minimum acidity and a high total soluble solids, total and reducing sugars. But there were no comparable changes in protein and ascorbic acid contents, due to treatments.

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