Biogenesis of Banana Volatiles

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Over 150 volatile compounds have been identified in bananas by various investigators. Most of the components are aliphatic esters, alcohols, and carbonyls. The flavor compounds are produced in the postclimacteric ripening phase in a cyclic manner. Biogenetic pathways for the development of banana volatiles have been established in a series of radiolabeling experiments. [^{14}C]Leucine and [^{14}C]valine were converted into the corresponding methyl-branched esters, alcohols, and acids. Some related phenolic ethers, such as eugenol, eugenol methyl ether, and elimicin were formed by the conversion of [^{14}C]phenylalanine. Radiolabeled fatty acids (C_2–C_{10}) were converted into the corresponding alcohols, esters, and ketones. The experiments were performed with postclimacteric banana tissue slices. The distribution of radiolabeling in the volatile compounds was determined by radio gas chromatography. [^{14}C]Linoleic acid and [^{14}C]linolenic acid were converted to hexanal, *trans*-2-hexenal, and 12-oxododecenoic acid by ripening bananas. Unripe bananas formed 2-nonenal, 2,6-nonadienal, and 9-oxononanoic acid from the same fatty acids. Possible biogenetic pathways are discussed.

PRODUCTION OF VOLATILES DURING RIPENING OF BANANAS

The typical flavor compounds of fruits like bananas, apples, and pears are not produced during growth, nor are they present at the time of harvest. Flavor compounds in these fruits are produced during a short ripening period related to the climacteric rise in respiration (Drawert *et al.*, 1969; Heinz *et al.*, 1965; Paillard, 1968; Romani and Ku, 1966; Tressl *et al.*, 1970a). The preclimacteric fruit produces small amounts of ethylene, which is recognized as a "ripening hormone," and induces biochemical, physical, and chemical changes in color, texture, the permeability of membranes, and an increase in some proteins and enzyme activities (Biale, 1964; Hansen, 1966; Palmer, 1971). One of these biochemical changes is the production of flavor compounds.

Figure 1 shows the production of some banana volatiles during storage. The upper curve shows the respiration of the bananas at a storage temperature of 15°. The climacteric rise is reached after 5 days. The diagram shows the development of some flavor compounds of the variety Gros Michel. Sequential 300-g samples of bananas were homogenized with methanol to inhibit the fruit enzymes. The homogenate was extracted for 8 hr with pentane–methylene chloride (2:1), with the addition of an internal standard, and the concentrated aroma extract was investigated by gas chromatography. The esters are produced in the postclimacteric ripening phase. Some of the curves exhibited a slight cyclic manner.

Tressl and Jennings (1972) developed an enrichment technique for studying the production of volatiles continuously without destruction of the fruits. Sequential samples of air swept through a chamber containing ripening bananas and incorporating internal standards were trapped on Porapak Q and recovered for gas chromatographic analyses. Peak areas, determined with digital integration and corrected for recovery of internal standard, show that the volatiles are produced in the postclimacteric ripening phase. The acetate and butyrate esters are produced at rates that vary in a cyclic manner (Tressl and Jennings, 1972). Figure 2 shows that a ripening fruit is a highly dynamic system, with short-term fluctuations in relative amounts of individual compounds. This method has the advantage that the fruits are not destroyed during sampling of the volatiles, and provides an essence with no solvent and a minimum amount of water.

Although the acetate and butyrate esters are most abundant in the bananas, some 3-methylbutyrates, 2-methylpropionates, and caproates are also produced in minor amounts. Besides the aliphatic esters, banana aroma concentrates possess some primary and secondary alcohols, some ketones and aldehydes, and five to six related phenolic ethers (Murray *et al.*, 1968; Wick *et al.*, 1966, 1969; Tressl *et al.*, 1970b).

METABOLIC PATHWAYS PRODUCING BANANA VOLATILES

Biogenesis of the many different individual banana volatiles can be explained by a few known metabolic pathways. We would like to point out some pathways by which many of the known banana aroma compounds are probably produced: conversion of some amino acids like leucine and valine into methyl-branched alkyl and acyl compounds of esters and into methyl-branched alcohols; production of acids, alcohols, esters, and ketones *via* fatty acid metabolism; and enzymatic oxidative splitting of linoleic and linolenic acid into C_6 and C_9 aldehydes and C_9 and C_{12} oxo acids. We have investigated these postulations with ^{14}C-labeled precursors and banana tissue slices. In labeling experiments, banana tissue slices in different ripening stages were incubated with ^{14}C-labeled precursors (10–50 μCi) in 0.4 *M* sucrose solution. After an incubation period of 3 to 5 hr, the slices were separated from the solution, washed, homogenized with methanol, and extracted for 8 hr with pentane–methylenechloride (2:1) or pentane–ether (1:1). The extract was carefully concentrated to a volume of 0.25 ml. Aliquot samples of the radioactive extract were investigated by gas chromatographic isolation of individual compounds and measurement of the radioactivity by liquid scintillation and by radio gas chromatography. Both methods showed similar results.

CONVERSION OF SOME AMINO ACIDS

L-**Leucine.** Many of the major banana aroma components are branched-chain esters and alcohols (Tressl *et al.*, 1970b,d; Wick *et al.*, 1969). The 3-methylbutyl esters, the 3-methylbutyrates, and 3-methyl-1-butanol might be derived from leucine. The 2-methylpropyl esters, the 2-methylpropionates, and 2-methylpropanol-(1) might be derived from valine. Leucine and valine were known to accumulate in ripening bananas (Palmer, 1971; Wick *et*

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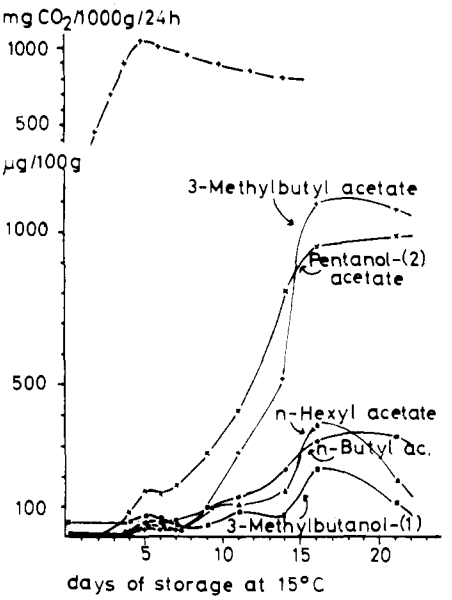

Figure 1. Production of some banana volatiles by the variety Gros Michel during storage at 15°.

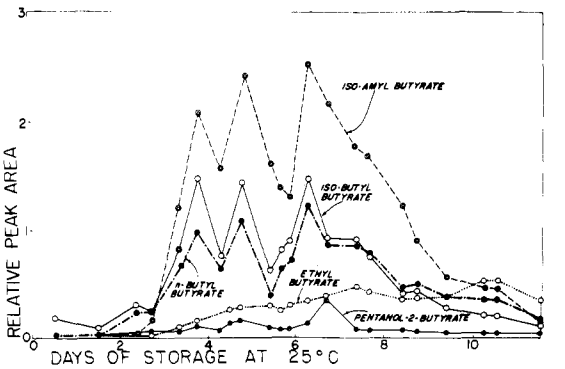

Figure 2. Individual butyrate esters from sequential samples of the emanations from ripening Valery bananas.

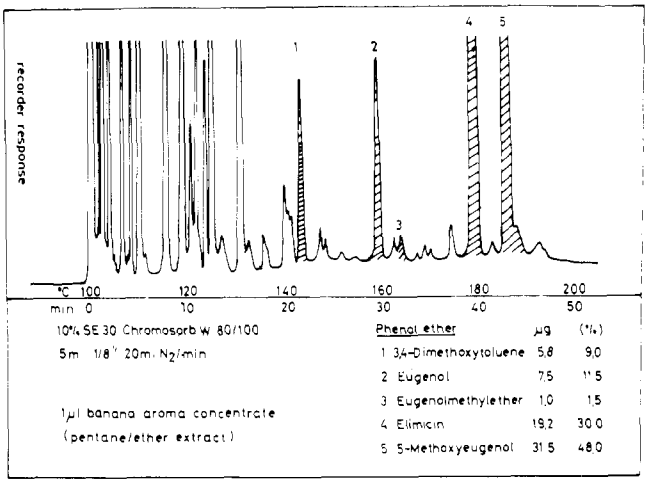

Figure 3. Gas chromatographic separation of an aroma concentrate from ripe banana fruit.

al., 1966). Wyman *et al.* (1964) and Myers *et al.* (1969, 1970) demonstrated the transformation of [^{14}C]leucine to 3-methyl-1-butanol and 3-methylbutyl acetate by banana disks. We investigated the free amino acids in ripening bananas. After the climacteric rise in respiration, the amounts of L-leucine and L-valine increased from 5 to 15 mg per 100 g. L-Isoleucine and other amino acids remained constant. There seems to be a correlation between the increase in the amount of leucine and valine and the production of flavor components. Isoleucine, which is only a precursor for some minor aroma components, remained constant (Drawert *et al.*, 1973b).

Labeling experiments using postclimacteric banana tissue slices and ^{14}C-labeled amino acids showed that [^{14}C]leucine was converted by banana tissue slices into 3-methyl-1-butanol, 3-methylbutyl esters, 3-methylbutyrates, and 2-ketoisocaproate. The results are shown in Table I. The distribution of radioactivity among 13 gas chromatographic fractions was measured by liquid scintillation. Larger proportions of radioactivity were found in 3-methylbutyl esters and 3-methylbutyrates. The activity in butyl butyrate and 2-pentanol butyrate (fraction 8) can not be explained. Hydrolyses of the aroma extract showed nearly equal distribution of activity in alcohols and acids. By far the largest proportion of radioactivity was found in 3-methyl-1-butanol. The labeling in the 2-heptanol fraction might be explained by branched 2-heptanol, which was identified by Wick *et al.* (1969). 2-Ketoisocaproic acid and 3-methylbutyric acid showed 97% of the radioactivity in the acid fraction.

L-Valine. Labeling experiments with postclimacteric banana tissue slices and [U-^{14}C]-L-valine showed an analogous conversion of the amino acid into 2-methyl-1-propanol (4.5%), 2-methylpropyl acetate (14%), 2-methylpropionic acid (45%), and 2-ketoisovaleric acid (22%), besides some other components (Tressl *et al.*, 1970c).

L-Phenylalanine. Besides leucine and valine, phenylalanine also increased during ripening of bananas. Phenylalanine was supposed to be a precursor of phenolic ethers and β-phenylethanol. Some related phenolic ethers of banana like eugenol, eugenol methyl ether, and elimicin were first identified by Wick *et al.* (1966). 3,4-Dimethoxytoluene and 5-methoxyeugenol were identified by infrared and mass spectra in our laboratory. Figure 3 shows a gas chromatogram of a pentane–ether extract from postclimacteric bananas. Elimicin and its precursor, 5-methoxyeugenol, are present in large amounts. Next to 3-methylbutyl acetate, 5-methoxyeugenol is the most abundant compound in the banana aroma concentrate. We believe this is the first time that this compound has been found in natural products.

Figure 4 shows a possible pathway which may explain the production of these compounds in bananas. Some of the enzymes involved were found and isolated recently (Pridham, 1965; Russel and Conn, 1969; Shimida *et al.*, 1970; Vanghan and Butt, 1969). Labeling experiments with banana tissue slices and [1-^{14}C]phenylalanine (chains labeled) showed labeling of the phenolic ethers with an allyl system. [1-^{14}C]Caffeic acid was converted into eugenol, eugenol methyl ether, and elimicin by banana disks. The results are shown in Table II. Eugenol accounts for 53% of the activity in the aroma extract of the sucrose solution and 5-methoxyeugenol accounts for about 10%. Eugenol methyl ether and elimicin are better labeled in the aroma extract of the banana disks. The results show some analogy to the labeling experiments with [2-^{14}C]caproate and [8-^{14}C]carpylate, which will be discussed later. We found reduction of the acids to alcohols in the sucrose solution controls and in the banana disks. We found transformation of the acids into esters only in the banana disks.

The results of labeling experiments with banana tissue slices and [2-^{14}C]phenylalanine are summarized in Table III. β-Phenylethanol and the esters are minor components of the banana. The conversion of phenylalanine into β-phenylethanol is an analogous reaction to the transformation of leucine and valine into the corresponding alcohols.

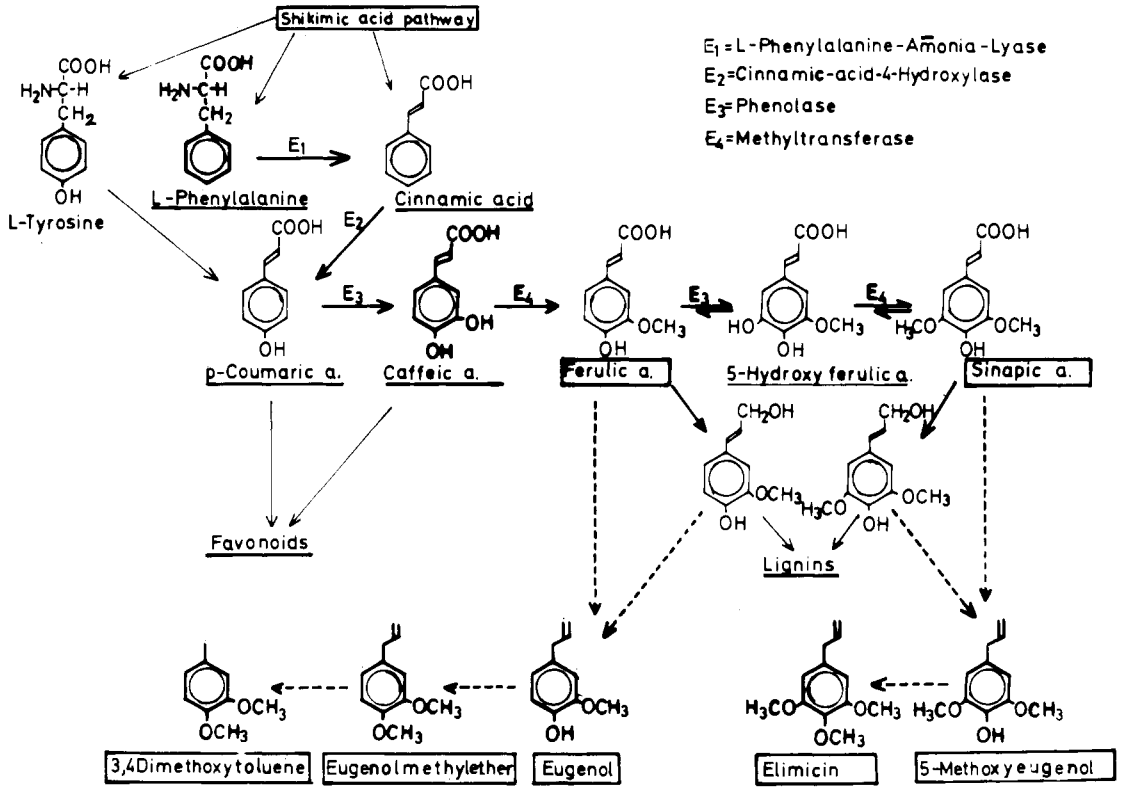

Figure 4. Scheme of pathways for formation of phenol ethers in banana.

Table I. Conversion of [U-^{14}C]-L-Leucine into Volatile Components by Postclimacteric Banana Tissue Slices

Banana disks	40 g (3 × 20 mm)
Incubation time	3 hr
Precursor	50 μCi of [U-^{14}C]leucine
Radioactivity in the aroma extract, %	0.5

Distribution of radioactivity among volatile components, %

Ethyl acetate	0.5
3-Methylbutanal	
2-Methylbutyl acetate	1.1
Methyl 3-methylbutyrate	
Ethyl butyrate	0.1
n-Butyl acetate	2.4
Ethyl *3-methylbutyrate*	
3-Methylbutyl acetate	*16.0*
3-Methyl-1-butanol	*18.0*
2-Methylpropyl *3-methylbutyrate*	*1.9*
3-Methylbutyl 2-methylbutyrate	
n-Butyl butyrate	10.0
2-Pentanol butyrate	
3-Methylbutyl butyrate	*10.0*
3-Methylbutyl 3-methylbutyrate	*9.0*
Methyl 2-ketoisocaproate	4.0
n-Hexyl butyrate	
3-Methylbutyl caproate	*25.0*
2-Heptanol *3-methylbutyrate*	
2-Heptenol *3-methylbutyrate*	
3-Methylbutyric acid	*2.0*

Distribution of radioactivity among volatile components after saponification of the aroma extract

Alcohols (47%)	%	Acids (53%)	%
2-Methyl-1-propanol	0	Acetic acid	0.1
1-Butanol	0	Butyric acid	1.7
3-Methyl-1-butanol	76.0	3-Methylbutyric acid	35.0
2-Heptanol	23.0	Caproic acid	1.2
1-Hexanol	1.0	2-Ketoisocaproic acid	62.0

Table II. Conversion of [1-^{14}C]Caffeic Acid into Phenolic Ethers by Banana Tissue Slices

Banana disks	50 g (3 × 20 mm)
Incubation time	5 hr

	Disks	Sucrose solution
Radioactivity in the pentane–ether extract, %	0.5	1.0
Radioactivity of nonmetabolized caffeic acid in the extract	0.45	0.90

Distribution of radioactivity among banana aroma components, %

Peaks eluted before eugenol methyl ether	6.0	7.0
Eugenol methyl ether	10.0	5.5
Eugenol	14.0	53.0
Elimicin	12.0	
5-Methoxyeugenol	6.0	10.5
Peaks eluted after 5-methoxyeugenol	52.0	24.0

PRODUCTION OF VOLATILES *VIA* FATTY ACID METABOLISM

Most unripe fruits (apples, bananas, strawberries, etc.) produce a variety of even and odd numbered fatty acids from C_1 to C_{20} and higher, some minor volatile compounds (*e.g.*, primary and secondary alcohols), and some C_6- and C_9-aldehydes. During ripening these fruits develop the ability to convert some of the acids into esters, ketones, and alcohols. We investigated the conversion of some ^{14}C-labeled acids by banana tissue slices.

Acetate and butyrate esters account for about 70% of the aroma compounds in banana aroma concentrate. The esters are produced in a cyclic manner, and the two cycles are apparently out-of-phase (Tressl and Jennings, 1972). The results of labeling experiments with [U-^{14}C]acetate and [1-^{14}C]butyrate are shown in Table IV. Postclimacteric banana slices incorporate [U-^{14}C]acetate only into acetate esters. Saponification of the radioactive aroma con-

Table III. Conversion of [2-^{14}C]-L-Phenylalanine into Banana Aroma Components by Banana Tissue Slices

Banana disks	50 g (3 × 20 mm)
Incubation time	5 hr
Radioactivity in the aroma extract, %	0.56
Distribution of radioactivity among banana components, %	
β-Phenylethanol	67
Eugenol	
Eugenol methyl ether	
β-Phenylethyl acetate	23
β-Phenylethyl butyrate	10
Elimicin	
5-Methoxyeugenol	

Table IV. Conversion of [U-^{14}C]Acetate and [1-^{14}C]Butyrate into Volatile Components by Postclimacteric Banana Tissue Slices

Banana disks	40 g	40 g
Precursor (50 μCi)	[U-^{14}C]acetate	[1-^{14}C]butyrate
Incubation time	3 hr	3 hr
Radioactivity in the aroma extract, %	4.5	8.3
Distribution of radioactivity among volatile components, %		
Ethyl *acetate*	*7.7*	0.1
2-Methylpropyl *acetate*	*15.7*	0.1
Ethyl *butyrate*	0.4	*4.4*
n-Butyl *acetate*	*12.3*	0.8
2-Pentanol acetate	0.9	0.2
3-Methylbutyl *acetate*	*55.0*	2.3
1-Butanol		
2-Methylpropyl *butyrate*	0.7	*10.0*
Butyl *butyrate*	0.3	*6.3*
2-Pentanol *butyrate*		
3-Methylbutyl *butyrate*	0.2	*63.0*
2-Heptanol *acetate*	*5.2*	0.3
Hexyl *acetate*		
3-Methylbutyl 3-Methylbutyrate	1.4	1.0
2-Heptanol *butyrate*	0.2	*10.5*
Hexyl *butyrate*		
Butyric acid		1.0

centrate showed 99% of the activity in the acetate fraction. Acetate acylates the different alkyl compounds of the banana. In an analogous reaction, [1-^{14}C]butyrate is converted only into the corresponding butyrate esters (Tressl *et al.*, 1970d). The higher fatty acids (C_6, C_8, C_{10}) serve in a variety of ways as aroma precursors. We have shown these reactions with [2-^{14}C]hexanoate, [8-^{14}C]octanoate, and [10-^{14}C]decanoate when introduced into tissue slices. For identification of labeled esters, individual compounds were isolated by gas chromatographic trapping and, after saponification the alkyl and acyl fractions, were investigated by radio gas chromatography. The fatty acids were determined as methyl esters. The methods have been reported in detail (Tressl and Drawert, 1971).

Results of labeling experiments with [2-^{14}C]hexanoate are shown in Table V. [2-^{14}C]Hexanoate is reduced to 1-hexanol by climacteric and postclimacteric banana disks. Note that in this case about the same conversion to 1-hexanol occurred in the sucrose controls. The conversion of the fatty acid into esters could be demonstrated only with postclimacteric tissue slices. Labeling of methyl, ethyl, butyl, 3-methylbutyl, hexyl, and octyl caproate indicates acylation of the different alkyl compounds of banana. Labeling of hexyl acetate and hexyl caproate indicates acylation of 1-hexanol. There is a small conversion of the precursor into 2-pentanone and 2-pentanol. Most of the activity in the aroma extracts resided in nonmetabolized [2-^{14}C]hexanoate.

Table V. Conversion of [2-^{14}C]Hexanoic Acid into Volatile Components by Banana Tissue Slices

	Climacteric		Postclimacteric	
Banana disks	50 g (3 × 20 mm)		50 g (3 × 20 mm)	
Incubation time	5 hr		5 hr	
	Disks	Sucrose solution	Disks	Sucrose solution
Radioactivity in the aroma extract, %	20	13.5	23	7
Distribution of radioactivity among volatile components, %				
2-Pentanone	0.7	0.1	0.14	0.2
Valeric acid	0.1	0.1		0.2
Methyl caproate	0.2		0.11	0.3
Ethyl caproate			0.15	
n-Hexyl acetate	0.7		*2.1*	
1-Hexanol	*9.2*	*15.1*	*18.7*	*25.6*
Butyl caproate	0.1		*2.5*	0.1
Hexyl butyrate				
3-Methylbutyl caproate	0.2		*8.2*	0.2
Amyl caproate			0.1	
Ester (not identified)	0.1		*2.1*	
Hexyl caproate	*7.7*	0.1	*12.7*	0.5
Octyl caproate			1.3	
Caproic acid	81.0	84.6	51.9	72.9

Table VI. Conversion of [10-^{14}C]Decanoic Acid into Volatile Components by Banana Tissue Slices

	Climacteric		Postclimacteric	
Banana disks	50 g (3 × 20 mm)		50 g (3 × 20 mm)	
Incubation time	5 hr		5 hr	
	Disks	Sucrose solution	Disks	Sucrose solution
Radioactivity in the aroma extract, %	33.5	6	44	13.5
Distribution of radioactivity among volatile components, %				
Caproic acid		4	0.2	0.1
2-Nonanone				
Caprylic acid				
Pelargonic acid	2.5	2.4	1.3	3.1
Methyl decanoate			0.5	
Ethyl decanoate			1.5	
1-Decanol	4.0		7.1	0.7
Butyl decanoate			1.9	
iso-Amyl decanoate			17.2	
Hexyl decanoate			11.2	
Decanoic acid	93.5	93.6	59.1	96.1

[8-^{14}C]Octanoate is, in a similar manner, transformed into volatile components. The results have been reported in detail (Tressl and Drawert, 1971). [8-^{14}C]Octanoate is converted into 1-octanol and 4-hepten-2-ol by climacteric and postclimacteric banana disks. But the conversion of the precursor into octyl esters and octanoates could be demonstrated only with postclimacteric tissue slices. There was a small conversion of octanoate into 2-heptanone, 2-pentanone, hexanoic acid, and butyric acid involving β-oxidion.

Results of labeling experiments with banana tissue slices and [10-^{14}C]decanoate are shown in Table VI. [10-^{14}C]Decanoate is converted into some decanoates and reduced to 1-decanol. Labeling of pelargonic acid indicates

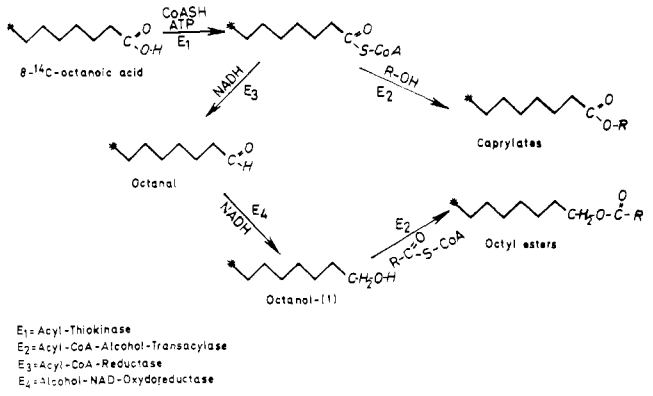

Figure 5. Reaction scheme for conversion of octanoic acid into esters.

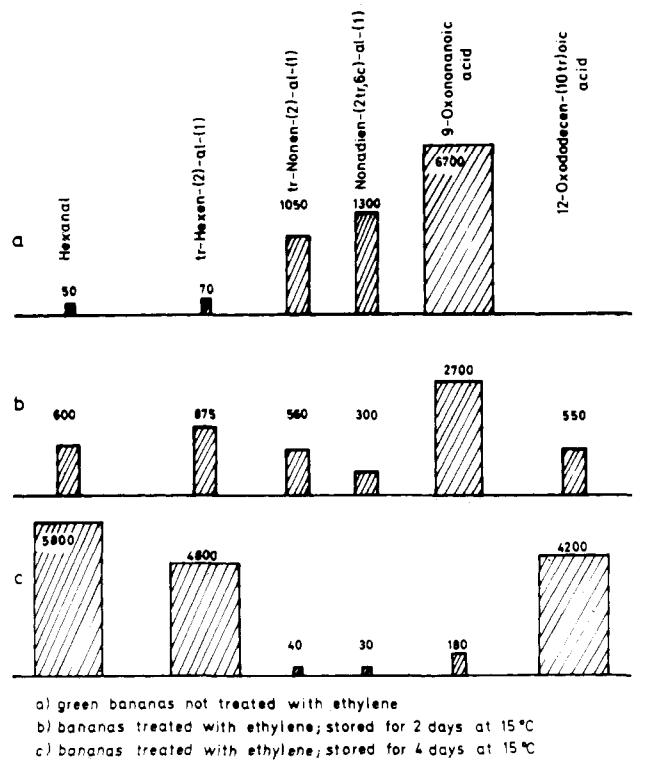

Figure 6. Enzymatic production of C_9 and C_6 aldehydes and C_9 and C_{12} oxo acids in homogenates of bananas.

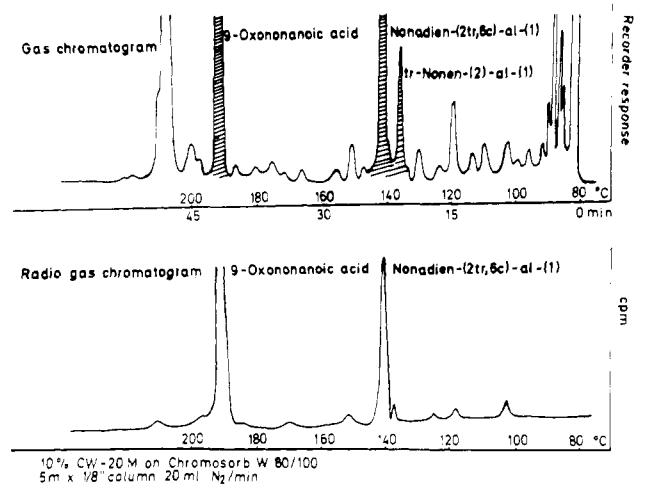

Figure 7. Enzymatic oxidative splitting of [U-^{14}C]linolenic acid by homogenates of green bananas.

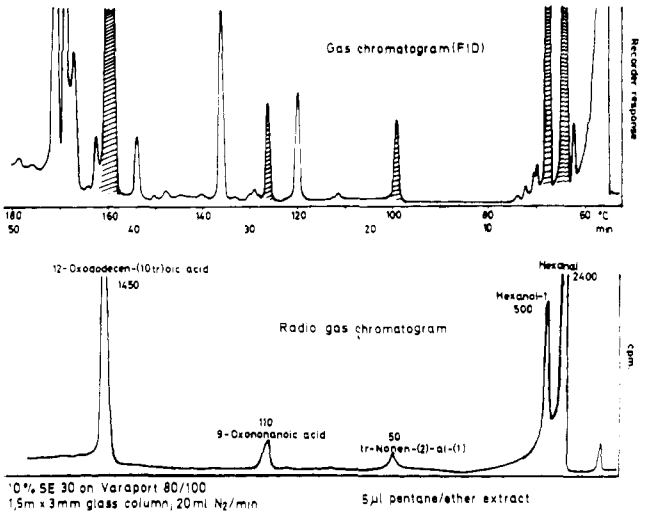

Figure 8. Enzymatic oxidative splitting of [U-^{14}C]linoleic acid by an enzyme extract of ripe bananas.

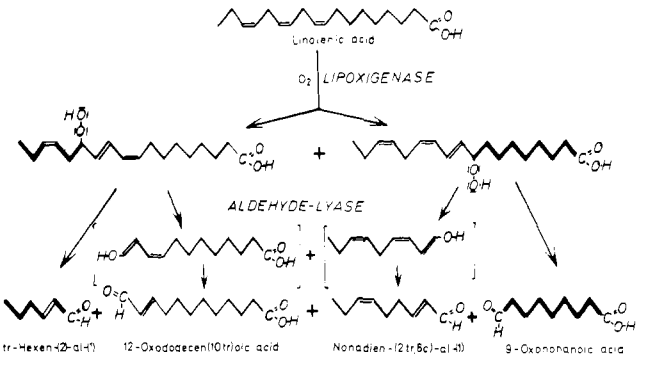

Figure 9. Reaction scheme for enzymatic splitting of linolenic acid into aldehydes and oxo acids.

α oxidation. [U-^{14}C]Palmitic acid was not converted into volatile constituents by banana tissue slices. Figure 5 shows a reaction scheme which may explain the transformation of fatty acids into alcohols and esters. Kolattukudy (1970b) discusses a similar pathway for the conversion of C_{14} to C_{18} fatty acids into wax esters. Fatty acid acyl CoA reductase was recently isolated and purified by Kolattukudy from *Euglena gracilis* (Kolattukudy, 1970a,b, 1971).

ENZYMATIC OXIDATIVE SPLITTING OF LINOLEIC AND LINOLENIC ACID INTO C_6 AND C_9 ALDEHYDES AND C_9 AND C_{12} OXO ACIDS

Drawert *et al.* (1966) reported the enzymatic formation of 2-hexenal and hexanal from linolenic and linoleic acid in banana, apple, pear, plum, and grape homogenates. Forss *et al.* (1962) identified *trans*-2-nonenal and *trans*-2,*cis*-6-nonadienal as typical aroma compounds in cucumbers. Fleming *et al.* (1968) showed the formation of C_9 aldehydes by an enzymatic reaction requiring O_2. Kazeniac and Hall (1970) and Stone *et al.* (1971) reported the conversion of [^{14}C]linolenic acid into *cis*-3-hexenal, *trans*-2-hexenal, and *cis*-3-hexenol by tomatoes. Apples and grapes produce only hexanal and hexenal when homogenized in air. When the fruit enzymes are inhibited there is no production of aldehydes (Drawert *et al.*, 1973a).

The production of aldehydes in banana homogenates depends on the ripening stage of the fruits. Peeled bananas were homogenized with methanol for 10 min and the homogenate was extracted with pentane–ether. The extract was investigated by gas chromatography. Only

small amounts of aldehydes and oxo acids were detected. In a similar experiment, peeled bananas were homogenized with buffer (0.1 *M* phosphate, pH 6.8). After 10 min the enzymes were inhibited with methanol and the homogenate was extracted and analogously investigated by gas chromatography. The results are shown in Figure 6. Green bananas, not treated with ethylene, produce *trans*-2-nonenal, *trans*-2,*cis*-6-nonadienal, and 9-oxononanoic acid. The carbonyl compounds produced by green bananas and cucumbers are identical. Bananas, treated with ethylene and stored for 4 days at 15°, produce hexanal, *trans*-2-hexenal, and 12-oxo-*trans*-10-dodecenoic acid. These carbonyl components are also produced by climacteric and postclimacteric bananas. Bananas treated with ethylene and stored for 2 days at 15° produce hexanal, *trans*-2-hexenal, 12-oxo-*trans*-10-dodecenoic acid, *trans*-2-nonenal, *trans*-2,*cis*-6-nonadienal, and 9-oxononanoic acid to nearly equal amounts. The carbonyl components were identified by their infrared and mass spectra in our laboratory. The results will be published in detail in the near future (Tressl *et al.*, 1973). The carbonyl compounds are potent flavor components with low olfactory thresholds. Their production during processing of fruits causes changes in flavor. The changes may be desirable or undesirable, depending on the product.

Linolenic and linoleic acid were presumed to be precursors of the carbonyl compounds. Investigation with bananas and apples showed a correlation between the production of aldehydes and a decrease in the amounts of linoleic and linolenic acid. The conversion of labeled linoleic and linolenic acid into C_6 and C_9 aldehydes was shown with banana homogenates. The distribution of the radioactivity among volatile components was investigated by radio gas chromatography. The results of the enzymatic oxidative splitting of [U-^{14}C]linolenic acid by homogenates of green bananas, providing labeled nonadienal and labeled 9-oxononanoic acid, are shown in Figure 7.

Attempts to isolate the enzyme system responsible for the production of aldehydes failed. Acetone destroyed the activity. Lipoxigenase preparations did not produce C_6 or C_9 aldehydes like fruit homogenates. However, a crude enzyme preparation showed high activity for aldehyde production. [U-^{14}C]Linoleic acid is converted by the enzyme extract of ripe bananas into hexanal, hexanol, and 12-oxo-*trans*-10-dodecenoic acid. The results are shown in Figure 8.

Radiolabeled 13- and 9-hydroperoxy octadecadienoic acid were transformed into C_6 and C_9 aldehydes and the corresponding oxo acids by the enzyme extract.

A reaction scheme which may explain the production of C_6 and C_9 aldehydes and C_9 and C_{12} oxo acids by bananas is shown in Figure 9. In the first step linolenic acid is transformed into the 13- or 9-hydroperoxy acid by lipoxigenase. These intermediate products might be split into aldehydes and oxo acids by an enzyme we called aldehyde lyase. The results will be reported in detail in the near future.

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LITERATURE CITED

Biale, J. B., *Science* **146,** 880 (1964).
Drawert, F., Heimann, W., Emberger, R., Tressl, R., *Justus Liebigs Ann. Chem.* **694,** 200 (1966).
Drawert, F., Heimann, W., Emberger, R., Tressl, R., *Z. Lebensm. Unters. Forsch.* **140,** 65 (1969).
Drawert, F., Tressl, R., Heimann, W., Emberger R., Speck, M., *Chem. Mikrobiol. Technol. Lebensm.* in press (1973a).
Drawert, F., Rolle, K., Heimann, W., Emberger, R., Tressl, R., *Z. Lebensm. Unters. Forsch.* in press (1973b).
Fleming, H. P., Cobb, W. Y., Etchells, I. L., Bell, T. A., *J. Food Sci.* **33,** 572 (1968).
Forss, D. A., Dunstone, E. A., Ramshaw, E. H., Stark, W., *J. Food Sci.* **27,** 90 (1962).
Hansen, E., *Annu. Rev. Plant Physiol.* **17,** 459 (1966).
Heinz, D. E., Creveling, R. K., Jennings, W. G., *J. Food Sci.* **30,** 641 (1965).
Kazeniac, S. J., Hall, R. M., *J. Food Sci.* **35,** 519 (1970).
Kolattukudy, P. E., *Arch. Biochem. Biophys.* **142,** 701 (1971).
Kolattukudy, P. E., *Biochemistry* **9,** 1075 (1970a).
Kolattukudy, P. E., *Lipids* **5,** 259 (1970b).
Murray, K. E., Palmer, J. K., Whitfield, F. B., Kennet, B. H., Stanley, G., *J. Food Sci.* **33,** 632 (1968).
Myers, M. J., Issenberg, P., Wick, E. L., *J. Food Sci.* **34,** 504 (1969).
Myers, M. J., Issenberg, P., Wick, E. L., *Phytochemistry* **9,** 1963 (1970).
Paillard, N., *Fruits* **23,** 383 (1968).
Palmer, J. K., in Hulme, A. C., Ed., "Biochemistry of Fruits and Their Products," Vol. 2, Chapter 2, Academic Press, London, 1971.
Pridham, J. B., *Annu. Rev. Plant Physiol.* **16,** 13 (1965).
Romani, R. J., Ku, L., *J. Food Sci.* **31,** 558 (1966).
Russel, D. W., Conn, E. E., *J. Biochem.* **113,** 109 (1969).
Shimida, M., Yamazaki, T., Higuchi, T., *Phytochemistry* **9,** 1 (1970).
Stone, E. J., Hall, R. M., Kazeniac, S. J., 162nd National Meeting of the American Chemical Society, Washington, D.C., September 1971.
Tressl, R., Drawert, F., *Z. Naturforsch.* **266,** 774 (1971).
Tressl, R., Drawert, F., Heimann, W., *Z. Lebensm. Unters. Forsch.* **142,** 249 (1970a).
Tressl, R., Drawert, F., Heimann, W., Emberger, R., *Z. Lebensm. Unters. Forsch.* **142,** 313 (1970b).
Tressl, R., Emberger, R., Drawert, F., Heimann, W., *Z. Naturforsch.* **246,** 704 (1970c).
Tressl, R., Emberger, R., Drawert, F., Heimann, W., *Z. Naturforsch.* **246,** 893 (1970d).
Tressl, R., Drawert, F., Speck, M., in preparation (1973).
Tressl, R., Jennings, W. G., *J. Agr. Food Chem.* **20,** 189 (1972).
Vanghan, P. F. T., Butt, V. S., *Biochem. J.* **113,** 109 (1969).
Wick, E. L., McCarthy, A. I., Myers, M., Murray, E., Nursten, H., Issenberg, P., *Advan. Chem. Ser.* **56,** 241 (1966).
Wick, E. L., Yamanishi, T., Kobayashi, A., Valenzuela, S., Issenberg, P., *J. Agr. Food Chem.* **17,** 751 (1969).
Wyman, H., Buckley, E. H., McCarthy, A. I., Palmer, J. K., Annual Research Report, United Fruit Co., 1964.

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