The resolution of the two fungicides is generally satisfactory. Only when small amounts of propiconazole were present with large concentrations of etaconazole may evaluation give some problems. Good results were obtained by using tangent skimming and peak height for evaluation. No further attention has been paid to this fact as in practice simultaneous or alternating application of these fungicides is not recommended. As much more important we considered the selectivity of our method against other pesticides with recommended application on the same crops as propiconazole and etaconazole.

A series of important pesticides which theoretically can be detected by a nitrogen–phosphorus-selective detector were investigated. All compounds mentioned in Table IV were mixed with the two fungicides and injected into the gas chromatograph. None interfered with propiconazole and etaconazole. The mixture was also chromatographed on the proposed alumina column. Most of the compounds were either retained or eluted completely in the fore cut.

The analysis procedure described was applied to the routine analysis of these fungicides in different crops: apples, pears, grapes, prunes, peaches, oranges, wheat and barley (grain and straw), soil, and water were analyzed. The samples were from supervised trials. The analyses were performed with no difficulties and no interferences were observed. Only straw samples needed an additional gel permeation cleanup in order to be clean enough for the final determination. This cleanup is also recommended for oily or fatty samples. Recoveries obtained were in the range of 76–100%. We therefore consider this method to be suitable for the determination either of propiconazole or of etaconazole. The simultaneous determination of the two fungicides is also possible, although they should only exceptionally be found on the same crop.

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Effects of Phosphorus, Potassium, Dolomite, and Nitrogen Fertilization on the Quality of Soybean. Yields, Proteins, and Lipids

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Effects of phosphorus, potassium, dolomite, and nitrogen fertilization upon yield, protein, and lipid contents of soybean var. "Davis" were investigated. Ground rock phosphate (0, 150, and 300 kg/ha), potassium chloride (0, 50, 100, and 150 kg/ha), and dolomite (0, 250, and 500 kg/ha) were applied, showing a significant ($p < 0.01$) positive response with yield. Urea was applied at rates ranging from 0 to 133 kg/ha but no change in yield was observed. Maximum yield (3300 kg/ha) was obtained with 150 kg/ha phosphate, 100 kg/ha potassium chloride, and 500 kg/ha dolomite. When the fertilizer amount was raised, an increase with phosphorus and a decrease with potassium were observed for protein content while an increase with phosphorus, potassium, and dolomite was observed for oil content. An interrelationship exists between the four main fatty acids for some fertilizer treatments. A positive correlation between linoleic and linolenic and a negative correlation between linolenic and oleic acids were observed.

Research has played in the last 20 years an important role in making soybean the premier of oilseed protein and the dominant vegetable oil in the world. Leng (1973) pointed out the potential of tropical countries to become soybean producers. Yields over 3000 kg/ha could be obtained in these countries, but some limiting factors existed such as the need for suitable varieties and the use of adequate cultural production practices (Lam-Sanchez, 1981). The problem of adapted varieties is almost solved in some countries but the research to improve the quality of soybeans has been limited. The ideal soybean would be (a) high in protein and (b) high in oil. The oil should contain low levels of fatty acids, which cause stability problems. It is generally accepted that the linolenic acid content of the oil is responsible for flavor problems that limits its acceptance for use in cooking and frying (Dutton et al., 1951; Evans et al., 1971). It would be (c) low in indigestible carbohydrates and (d) low in antinutritional factors (Smith, 1981). The responses to fertilizer have often been inconsistent. In the past, in some areas, soybeans have had the reputation of not responding to fertilizer (Nelson, 1971). Nitrogen can be supplied by a proper symbiosis with the nitrogen fixed by *Rhizobium japonicum*, and in Mississippi, atmospheric nitrogen was fixed to levels of 180 kg/ha (Hinson and Hartwig, 1977). The effects of inoculation and N fertilizer on soybean var. "Clark" were studied (Haque et al., 1980), and the influence of N nutrition on total N, nitrate, and carbohydrate levels was studied by Brevedan et al. (1977). The use of lime in soybean production is a common practice which, besides raising soil pH to proper levels for an adequate symbiosis (pH 5.8–7.0), provides the ions Ca^{2+} and Mg^{2+} and removes Al^{3+} and Mn^{2+} into less toxic forms (Lam-Sanchez, 1981). The response of soybean to potassium fertilizer (Chevalier, 1977) has been undertaken, and attention must be given

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Table I. Soil Chemical and Physical Characteristics

soil depth, cm	pH		sand, %	silt, %	clay, %	organic matter, %				phosphorus, ppm		cations, mequiv/100 g				cation-exchange capacity, mequiv/100 g
	water	KCl				total	carbon	nitrogen	C/N ratio	total	available	Ca	Mg	K	Na	
0-20	5.80	5.35	54.0	25.8	18.0	2.16	1.26	0.11	11	687	20	2.38	0.15	0.14	0.11	5.18
20-50	5.25	4.95				1.16	0.68	0.04	17	723	14	0.75	0.03	0.03	1.04	3.07
50-100	5.40	6.10				0.53	0.31	0.02	15	996	38	0.34	0.06	0.02	0.06	1.73
100-180	5.50	6.05				0.34	0.20	0.02	12	1305	171	0.36	0.03	0.02	0.02	1.72

Table II. Effect of Phosphorus Fertilizer upon Yields and Oil and Protein Contents

experiment[a]	applied P_2O_5, kg/ha[b]		yield,[d] kg/ha	oil content,[e] %	protein content,[e] %
	1973-1974	maintenance[c]			
1	0	0	500[f]	17.78	36.66
2	90	0	650[f]	17.06	37.56
3	90	45	1500	18.05	38.81
4	90	90	2050	18.86	40.81
5	180	0	750[f]		
6	180	45	1650		
7	180	90	2250		
8	360	0	950[f]		

[a] Each experiment received 45 kg/ha N, 60 kg/ha K_2O, and 250 kg/ha dolomite, before harrowing. [b] Ground rock phosphate. [c] Every year since 1974-1975. [d] Mean of six replicates at 13% bean moisture. [e] Mean of three replicates. [f] Dry weight basis. Mean of four replicates.

to local sources of elements such as phosphorus (Lam-Sanchez, 1981). There is still a need for local research on this topic, which will consider the type of soil, the climatic factors, and the soybean variety in order to improve the field production, the protein, and oil qualities of soybeans.

Soybean var. "Davis" has recently been introduced into Madagascar and a large program of production (76000 ha) must be undertaken for protein and oil production. The purpose of this work was to investigate the effects of phosphorus, potassium, dolomite lime, and nitrogen fertilization on the quality of this soybean variety. This paper will discuss the results obtained upon yields, protein, and oil contents. The influence of fertilization was also investigated in connection with the fatty acid levels contained in these oils.

MATERIALS AND METHODS

Plots and Treatments. Field plots were located at Ampangabe (20 km from Antananarivo, within the highlands of Madagascar, 1400-m altitude). The experimental plots were 5 × 7 m with 1.0- and 1.5-m spaces between plots and replications, respectively. The design was a randomized block of two, three, or six replicates for each treatment. The chemical and physical characteristics of soil used in this investigation are listed in Table I. Rainfall in millimeters for the 1980–1981 growing season at this location was as follows: November, 35; December, 279; January, 247; February, 306; March, 394; April, 40. Among the soybean varieties from the world's collection, surveyed by several investigators (Collins and Howell, 1957; Collins and Sedgwick, 1959; White et al., 1961; Rinne and Seif, 1978), we have chosen soybean [*Glycine max* (L.) Merr] variety "Davis". Soybeans grew during the 1980–1981 season. The plots were seeded at a 10-cm depth, in 40-cm rows (density 250000 plants/ha) at mid-December. Soil temperatures at this location range from 24 to 29 °C at a 10-cm depth. The seeds were not inoculated with *Rhizobium japonicum*, but the presence of nodulated plants (12–13 nodules/plant) was observed and might be due to either soybean previously been planted or infected by indigenous rhizobia and rhizobia carried by seed. All experiment plots have received the nitrogen–phosphorus–potassium–dolomite basal fertilizer application expected for variable element in each experiment: 100 kg/ha urea (45 kg of N), 150 kg/ha ground rock phosphate (45 kg of P_2O_5), 100 kg/ha potassium chloride (60 kg of K_2O) and 500 kg/ha dolomite (30% MgO, 20% CaO), as indicated in Tables II–V. Plots used for the study of phosphorus effect have received 0–360 kg/ha P_2O_5 during the 1973–1974 season and 0–90 kg/ha P_2O_5 every year since 1974 as shown in Table II. Plots used for the study of potassium effect have received 0–90 kg/ha K_2O during 1976–1980 seasons as indicated in Table III. Plots used for the study of dolomite effect have received 0–2000 kg/ha dolomite in 1975 as shown in Table IV. Nitrogen was applied before sowing or 40 days after planting (DAP) as indicated in Table V. Weeding was done as necessary and plants were sprayed at flowering to control insects.

Beans were harvested 20 weeks after planting and the soybean seeds were reduced to 13% moisture level for yield determination.

Oil Extraction and Protein Determination. The soybean seeds at 13% moisture level were ground with a

Table III. Effect of Potassium Fertilizer upon Yields and Oil and Protein Contents

experiment[a]	applied K_2O, kg/ha[b]			yield,[c] kg/ha	oil content,[c] %	protein content,[c] %
	1976-1979	1979-1980	1980-1981			
9	0	0	0	450	17.29	46.25
10	30	0	0	650		
11	30	30	0	850		
12	60	60	0	1750		
13	30	30	30	1700	18.69	41.12
14	60	60	30	1900		
15	60	60	60	2350	19.21	38.14
16	90	90	90	2350	21.00	37.62

[a] Each experiment received 45 kg/ha N, 45 kg/ha P_2O_5, and 250 kg/ha dolomite before harrowing. [b] Potassium chloride. [c] Dry weight basis. Mean of three replicates.

Table IV. Effect of Dolomite Fertilizer upon Yields and Oil and Protein Contents

experiment[a]	applied dolomite, kg/ha 1975	1980–1981	yield,[b] kg/ha	oil content,[c] %	protein content,[c] %
17	0	0	200	18.55	40.25
18	2000	0	1650		
19	500	250	2300	19.19	38.75
20	500	500	2400		
21	2000	250	2600		
22	2000	500	2700	20.00	38.69

[a] Each experiment received 300 kg/ha P_2O_5 in 1975 and 45 kg/ha N, 45 kg/ha P_2O_5, and 60 kg/ha K_2O in 1980–1981, before harrowing. [b] Mean of two replicates at 13% bean moisture. [c] Dry weight basis. Mean of two replicates.

Table V. Effect of Nitrogen Fertilizer upon Yields and Oil and Protein Contents

experiment[a]	applied N,[b] kg/ha before sowing	40 DAP[c]	yield,[d] kg/ha	oil content,[e] %	protein content,[e] %
23	0	0	3300	19.12	37.25
24	15	0	3500		
25	30	0	3250		
26	45	0	3250	17.89	39.04
27	60	0	3250		
28	0	45	3300	18.34	39.75

[a] Each experiment received 45 kg/ha P_2O_5, 60 kg/ha K_2O, and 250 kg/ha dolomite, before harrowing. [b] Urea. [c] DAP: days after planting. [d] Mean of six replicates at 13% bean moisture. [e] Dry weight basis. Mean of three replicates.

laboratory hammer mill and passed through a 100-mesh sieve. The milled soybeans were dried in an oven (100 ± 2 °C) and then extracted with a Soxhlet by using petroleum ether (40–60 °C). The micromethod described by Welch (1977) was also used for the estimation of oil content and the determination of fatty acid composition. Triplicate determinations were made on each sample. However, the values obtained by the micromethod were always slightly lower (1%) than with other extractions. Nitrogen was determined by a macro-Kjeldahl procedure, followed by a semimicrodistillation into a 2% boric acid solution with a mixed indicator (Markham, 1942). The factor 6.25 was used to convert nitrogen to protein.

Determination of Fatty Acid Composition. Fatty acid methyl esters composition was determined by transmethylation using 2% H_2SO_4 in methanol at 80 °C for 3 h. A Girdel series 300 gas chromatograph with flame ionization detector and a glass injector was used for the separation measurement of the fatty acid methyl ester peaks. The glass capillary column (45 m × 0.35 mm i.d.) was coated with carbowax 20 M (0.15-μm phase thickness). Temperatures were 190 °C for the column, 200 °C for detector, and 220 °C for inlet ovens. The flow rate of helium as the carrier gas was 5 mL/min. The fatty acid methyl esters were quantitated by peak area integration. Triplicate determinations were made on each sample. The equivalent chain length (ECL) obtained for fatty acid methyl esters were in good agreement with those previously obtained for a Carbowax 20 M glass capillary column (Gaydou et al., 1980).

Statistical Analysis. Analysis of variance was conducted and least significant differences at the 5% and 1% levels of probability estimated to the *F* test (variance ratio test: number of degrees of freedom associated with error mean square of plots and treatments) for significance of results (Dagnelie, 1975). The effects were called highly significant when $p < 0.01$ and significant when $p < 0.05$.

RESULTS AND DISCUSSION

Yield. The soil fertility as shown in Table I is poor because exchangeable bases and available phosphorus are in low amounts. The organic matter is relatively poor (2.2% at 0–20-cm and 1.2% at 20–50-cm depth) as well as the C/N ratio. The pH soil is rather low (Table I). Liming creates a more favorable environment, besides raising the soil pH to a satisfactory level (ph 5.8–7.0) for soybean production while supplying calcium and magnesium and turning aluminum and manganese into less toxic forms. The application of dolomite (magnesian lime) to the soil was done before harrowing, together with potassium, phosphorus, and nitrogen.

Fertilization effects upon yield are summarized in Tables II–V. Experiments 1–8 show the effect of P_2O_5 upon yield, and a highly significant increase from 500 to 2250 kg/ha was observed (Table II). The residual effect of the phosphorus treatment in the year 1973–1974 was observed in experiments 1, 2, 5, and 8. Plants which were phosphorus deficient were stunted with small leaves. A good response of soybeans to this fertilizer on this soil, which is low in available phosphorus, was observed. High yields of soybeans containing relatively large quantities of P were also observed by Henderson and Kamprath (1970), and a relatively large removal of phosphorus by the harvested beans reflected this fertility management (Hanway and Thompson, 1967).

Experiments 9–16 (Table III) show the effect of potassium upon yield. When added K_2O ranges from 0 to 90 kg/ha, a highly significant increase of the yield from 450 to 2350 kg/ha was observed. Yield did not increase when K_2O was added up to 60 kg/ha (experiment 16). Both phosphorus and potassium give a carry-over response.

When dolomite is not added, the lowest yield was obtained (200 kg/ha, experiment 17, Table IV). The quantity of dolomite that needs to be applied depends upon soil pH, the level of cation-exchange capacity, the levels of Ca^{2+}, Mg^{2+}, Al^{3+}, and Mn^{2+}, the organic matter content, etc. Dolomite applied in 1975 significantly increased the yield in soybeans as shown by experiments 17 vs. 18, 19 vs. 21, and 20 vs. 22 (Table IV). Dolomite applied in 1980–1981 significantly increased the yield and we have obtained 2300–2700 kg/ha for experiments 19–22.

The influence of nitrogen was investigated in experiments 23–28 (Table V) by adding none or 100 kg/ha urea (45 kg of N) before sowing and 40 DAP. No change upon yield was observed in these three trials, which stayed at 3300 kg/ha. Nitrogen, an essential element for soybeans, which is contained in large amounts, especially in seeds (Hanway, 1969), can be supplied either by the nitrogen fixing bacteria *R. japonicum* or chemical nitrogen. The presence of nodules was observed although the seeds were not inoculated with the bacteria. In Western Nigeria, Kang (1975) observed that inoculation alone appeared to be inadequate to supply nitrogen needs of the crop. Herath (1974) observed in Sri Lanka responses to nitrogen, with and without inoculation, up to 20 and 40 kg/ha nitrogen, but experiments in Kenya (Okalo and Zschernitz, 1971) and Brazil (Olsen et al., 1975) showed no significant responses to nitrogen application.

Protein and Oil. The commercial value of soybeans may be explained because they can be processed into edible oil and high-quality protein. Among the many factors in any plant growth, environment that may affect the metabolism and composition soil conditions require important

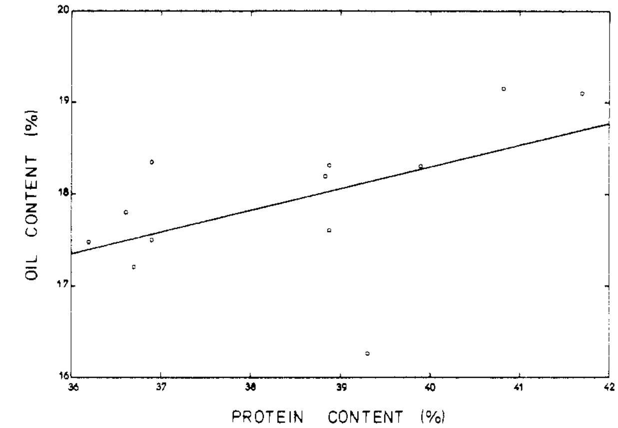

Figure 1. Oil and protein contents of soybean var. "Davis" for 12 experiments at various phosphorus fertilization levels.

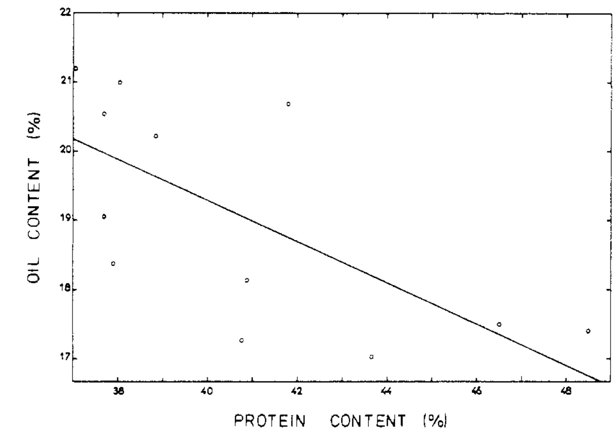

Figure 2. Oil and protein contents of soybean var. "Davis" for 12 experiments at various potassium fertilization levels.

consideration. The oil content and protein content for the various fertilization investigations are given in Tables II–V. The addition of phosphorus resulted in a significant and highly significant oil and protein content increases respectively for experiments 1–4 (Table II). The addition of potassium resulted in a significant oil content increase but resulted in a highly significant protein decrease. Dolomite fertilizer effect resulted in a significant oil increase but was not significant upon protein content. Nitrogen fertilizer was not significant upon oil and protein contents. Thus, it appears that the soybean quality is influenced by nutrient availability, phosphorus having a positive response upon oil and protein content, but potassium having a slightly negative response upon the protein content. Plots of the oil content vs. protein content give a positive relationship (Figure 1) with the 12 experiments investigated. The regression line ($p < 0.05$) fit for the data is

$$\text{oil} = 8.74 + 0.24\ \text{protein}$$

Plots of the oil content vs. protein content, for potassium fertilizer, give an inverse relationship (Figure 2) with the 12 experiments investigated, and the regression line ($p < 0.02$) fit for the data is

$$\text{oil} = 31.03 - 0.29\ \text{protein}$$

Such an inverse relationship was soon observed for 144 soybeans varieties (Hartwig and Lappas, 1979). These results show the direct influence of fertilization upon protein and oil levels of soybeans. In general, approximately 65% of the value of soybean is attributed to its protein content and 35% to soybean oil (Smith, 1981).

Fatty Acid Composition. The problem of soybean oil utilization as a vegetable oil is its flavor stability that limits

Table VI. Fatty Acid Composition of Soybean var. "Davis" Crude Oil

fatty acid[a]		composition[b]	
name	symbol	range, %	mean, %
tridecanoic	13:0	0.04–0.10	0.07
myristic	14:0	0.07–0.11	0.09
pentadecanoic	15:0	0.04–0.10	0.05
palmitic	16:0	10.88–12.48	11.51
palmitoleic	16:1ω7	0.09–0.18	0.15
stearic	18:0	2.45–3.89	2.85
oleic	18:1ω9	20.57–29.78	25.44
vaccenic	18:1ω7	2.71–4.00	3.27
linoleic	18:2ω6	42.06–52.71	48.45
linolenic	18:3ω3	6.61–9.44	7.52
arachidic	20:0	0.20–0.47	0.34
gadoleic	20:1ω9	0.19–0.47	0.27

[a] Determined as methyl esters on a glass capillary column coated with Carbowax 20 M at 190 °C. [b] Made upon 48 crude oil samples.

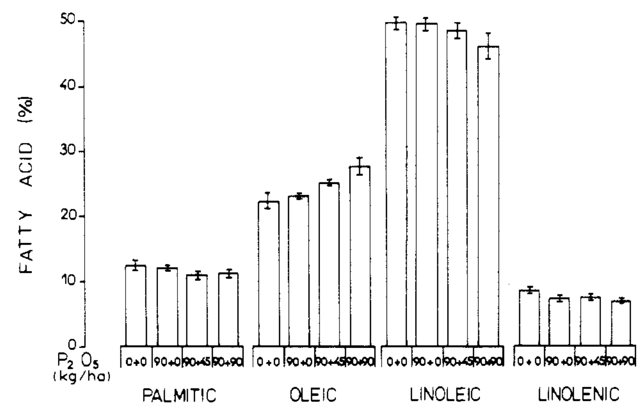

Figure 3. Effect of phosphorus fertilization on the fatty acid composition of soybean var. "Davis" crude oil. Errors bars represent standard deviations. For experimental conditions see Table II.

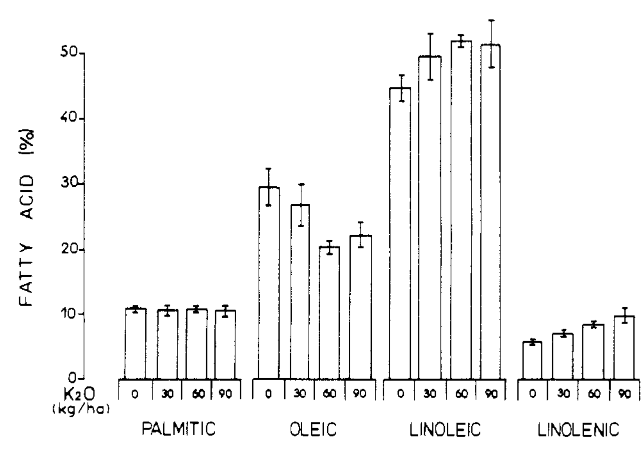

Figure 4. Effect of potassium fertilization on the fatty acid composition of soybean var. "Davis" crude oil. Errors bars represent standard deviations. For experimental conditions see Table III.

acceptance in cooking and frying (Evans et al., 1971). It is accepted that these flavor problems are in connection with the presence of linolenic acid in the oil. The various fatty acid and their ranges for all experiments investigated are given in Table VI. The values of palmitic acid range from 10.9% to 12.5%, the oleic acid values from 20.6% to 29.8%, the linoleic acid values from 42.1% to 52.7%, and the linoleic acid values from 42.1% to 52.7%, and the linolenic acid values from 6.6% to 9.4%. The change in level for these main fatty acids with various amounts of fertilizers are given in Figures 3–6. One can observe that

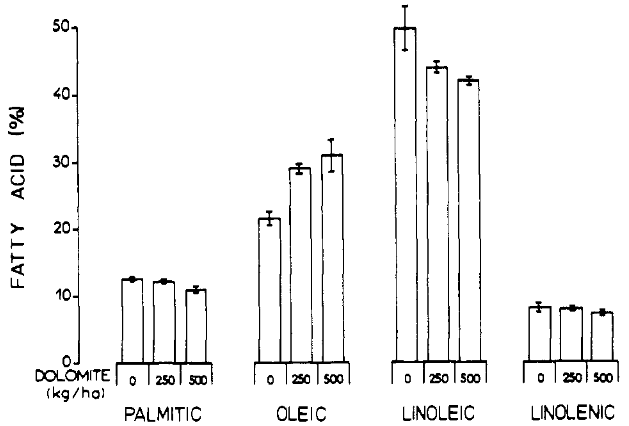

Figure 5. Effect of dolomite fertilization on the fatty acid composition of soybean var. "Davis" crude oil. Errors bars represent standard deviations. For experimental conditions see Table IV.

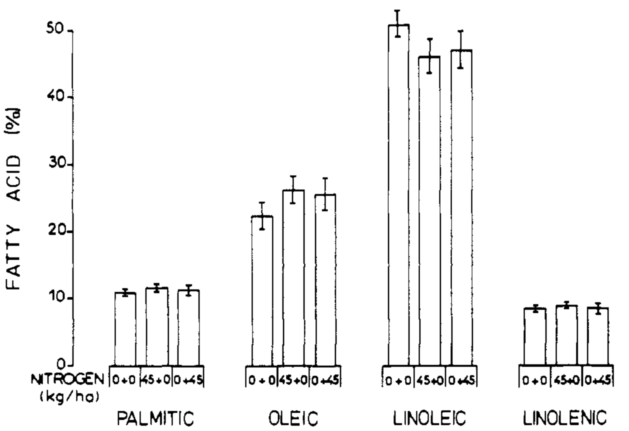

Figure 6. Effect of nitrogen fertilization on the fatty acid composition of soybean var. "Davis" crude oil. Errors bars represent standard deviations. For experimental conditions see Table V.

interrelationships exist between the four main fatty acids for each fertilizer treatment. There is a positive correlation between linoleic, linolenic, and palmitic acids. There is a negative correlation between linoleic and oleic acids. These results are in good agreement with the negative correlation observed between linolenic and oleic acids (White et al., 1961; Howell and Collins, 1957). The phosphorus fertilizer resulted in a highly significant increase of the oleic acid content from 22.1% to 27.3% (Figure 3). In the case of potassium fertilizer, the linolenic acids levels were significantly increased. Linolenic acid ranges from 6.6% to 9.8% when K_2O varies from 0 to 90 kg/ha (Figure 4). The oleic acid content was significantly decreased. The dolomite fertilizer has a highly significant decrease upon palmitic acid level (Figure 5).

These results show the fertilizer influence upon the fatty acid composition of soybeans, although it was said in previous work that oil composition was not influenced by the quality or the intensity of light, nitrogen, phosphorus, potassium, sulfur, trace elements, and manure of plant residues (Howell and Collins, 1957). Other environmental factors influencing fatty acid synthesis are high temperatures during pod filling, day length (Smith, 1981), geographical location, and irrigation (Chu and Sheldon, 1979). The biosynthesis of soybean oil by the plant depends upon the enzymes which are activated by nutrients coming from the soil, fertilizers, and planting location. On another way the genetic research to improve soybean oil quality has been undertaken for 30 years (Alderks, 1949). Linolenic acid levels in soybeans are controlled by four to five different genes (Howell et al., 1972); therefore, the genetic mechanism is complex and the genetic selection slowly improves. Such variation in the fatty acid composition of crude oils from the same variety, with various fertilizers, should be carefully controlled for the production of high-quality soybeans.

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Registry No. Dolomite, 16389-88-1; linoleic acid, 60-33-3; linolenic acid, 463-40-1; oleic acid, 112-80-1; palmitic acid, 57-10-3.

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