

COMPARATIVE FATTY ACID COMPOSITION OF LINSEED OIL PRODUCED IN NORTHERN AND SOUTHERN QUEENSLAND

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SUMMARY

Linseed oil from eight varieties of linseed grown at Walkamin (lat. 17°S.) and Hermitage (lat. 23° 21' S.) Research Stations was examined for iodine value (Wijs) and fatty acid composition. Palmitic (16:0), stearic (18:0), oleic (18:1) and linoleic (18:2) acids were produced in larger quantities by varieties grown at Hermitage, while linolenic acid (18:3) was produced in larger quantities by all varieties grown at Walkamin.

There was a significant positive correlation ($r = +0.97$) between percentage linolenic acid and iodine value, and a significant negative correlation ($r = -0.91$) between oleic and linolenic acids.

Introduction

Oil samples were obtained from cold-pressed seed of linseed varieties grown at Walkamin (lat. 17°S.) and Hermitage (lat. 23° 20' S.) Research Stations in 1965. An iodine value-refractive index relationship for these particular oils has been reported and the variability of iodine value with variety and district has been discussed (Price 1967). In this study it was observed that the varieties Bolley Golden, Viking and Hazeldean exhibited large differences in iodine value when grown in different districts. Since the iodine value is dependent directly on the degree of unsaturation of the oil, which in turn depends on the relative percentages of the constituent unsaturated fatty acids, it was felt desirable to determine the fatty acid composition of the oil samples from both districts. This paper presents the results of this study.

Material and Methods

Oil samples.—Samples of linseed seed were cold-pressed as previously described (Price 1967).

Iodine value (Wijs).—(a) Determined on cold-pressed oil as described by Mehlenbacher (1960, p. 311). (b) Calculated from fatty acid composition using the equation $100 \text{ iodine value} = (86 \times (18:1)\%) + (173.3 \times (18:2)\%) + (261.8 \times (18:3)\%)$.

Fatty acids.—Determined by gas liquid chromatography (G.L.C.) as methyl esters, using an Aerograph gas chromatograph Model 204B.

Methyl esters.—Esterification of oil samples (0.1 g) was achieved using boron trifluoride and methyl alcohol (BF_3/MeOH) by the method of Metcalf, Schmitz, and Pelka (1966), modified by extracting with hexane three times and removing excess hexane over anhydrous Na_2SO_4 at room temperature only. The final volume was adjusted to 20 ml.

Methyl ester standards.—Methyl palmitate, methyl linoleate and methyl linolenate were purchased as 99% pure. Methyl oleate was prepared from 90% pure oleic acid by esterification with BF_3/MeOH followed by column chromatography on acid-treated Florosil impregnated with silver nitrate (Willner 1965).

G.L.C. operating conditions.—The esters were separated on a 5 ft x $\frac{1}{8}$ in. stainless-steel column packed with 20% w/w diethylene glycol succinate (D.E.G.S.) on treated Embacel as the solid support. The Embacel was acid and solvent-treated and silanized using hexamethyl disilazane (H.M.D.S.) as outlined by Horning, Moscatelli, and Sweeley (1959). The packed column was conditioned for 36 hr at 190°C with a nitrogen flow rate of approximately 5 ml/min. The number of theoretical plates was measured and, using the relationship $n = 16 \left(\frac{t_r}{\Delta t} \right)^2$, was found to be approximately 1,000. This value n remained constant throughout the analysis period. Injector temperature was 190°C, column temperature 180°C, hydrogen flame ionization (F.I.D.) detector temperature 190°C. Nitrogen flow rate was 25 ml/min, hydrogen flow rate 25 ml/min.

Sample application.—Samples and standards ($3.35 \pm 0.1 \mu\text{L}$) were injected using a fixed-needle syringe. The total weight of sample injected did not exceed 25 μg and a linear detector response was obtained with all standards within the range 0–30 μg (Horning *et al.* 1964).

Area measurements.—Areas were measured by the peak height retention time product method of Bartlett and Iverson (1966). The sensitivity of 16:0, 18:1 and 18:2 esters in the F.I.D. were almost identical during any one day's

operation, being respectively 61.56, 61.23 and 61.57 area units μg^{-1} . The response of the F.I.D. to 18:3 ester was appreciably less, being 54.08 area units μg^{-1} . This was probably associated with decomposition of methyl linolenate on the column as reported by Gerson, Shorland, and McIntosh (1966), although D.E.G.S. as a stationary phase was not examined by these workers.

The analytical results for two samples injected on consecutive days are presented in Table 1.

TABLE 1
FATTY ACID PERCENTAGES ON CONSECUTIVE DAYS

Variety and Centre	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Injected
Bonnydoon, Walkamin ..	4.7	4.6	19.5	15.3	50.8	Day 1
Bonnydoon, Walkamin ..	4.7	4.7	19.7	15.3	50.6	Day 2
Bonnydoon, Hermitage ..	4.9	5.1	22.1	16.8	46.1	Day 1
Bonnydoon, Hermitage ..	4.9	5.2	22.4	16.4	46.1	Day 2

Results and Discussion

Figure 1 is a typical chromatogram of an esterified oil sample illustrating the degree of ester separation achieved using the operating conditions outlined above. Methyl linolenate was eluted after approximately 21 min.

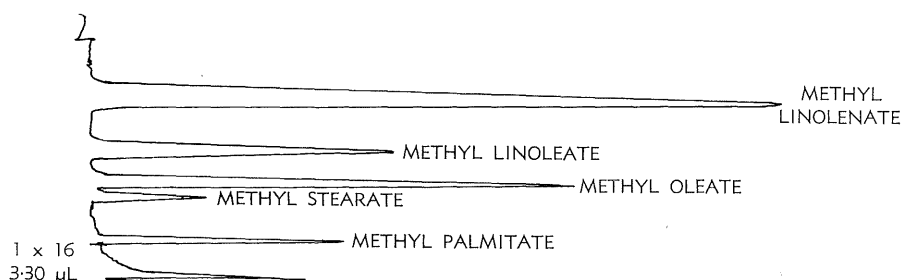


Fig. 1.—Typical chromatogram of an esterified oil sample.

Table 2 lists the constituent fatty acids in the oil from seed of eight linseed varieties grown at Walkamin and Hermitage in 1965. Also included are the determined and calculated iodine values for these samples.

Palmitic and stearic acids were the minor constituents, together totalling 7.97% (mean) at Walkamin and 8.84% (mean) at Hermitage. Oleic acid varied from 15.0 to 22.7% (mean 18.37%) at Walkamin and from 17.7 to 23.5% (mean 20.47%) at Hermitage. Linoleic was the minor unsaturated fatty acid (mean 12.41%) at Walkamin and (mean 14.36%) at Hermitage.

TABLE 2
FATTY ACID COMPOSITION AND IODINE VALUES OF SAMPLES FROM HERMITAGE AND WALKAMIN RESEARCH STATIONS, 1965

Variety	Origin	Palmitic Acid (16 : 0) (%)	Stearic Acid (18 : 0) (%)	Oleic Acid (18 : 1) (%)	Linoleic Acid (18 : 2) (%)	Linolenic Acid (18 : 3) (%)	Iodine Value (Wijs) (Determined)	Iodine Value (Calculated)
Dakota	Walkamin ..	3.9	2.5	19.2	13.3	56.1	187	186
	Hermitage ..	4.0	3.0	20.6	15.3	52.0	180	181
Newlands	Walkamin ..	4.3	3.4	19.2	12.2	56.0	183	184
	Hermitage ..	4.6	3.9	19.5	12.5	54.4	180	181
Viking	Walkamin ..	4.6	3.8	15.1	11.6	60.0	190	190
	Hermitage ..	4.7	5.0	19.0	14.7	51.6	175	177
Walsh	Walkamin ..	4.2	5.2	22.7	12.2	50.8	172	174
	Hermitage ..	4.6	5.9	23.5	14.0	47.0	166	168
Marine	Walkamin ..	3.5	2.5	17.2	12.0	59.8	193	192
	Hermitage ..	3.4	2.8	17.7	12.3	58.8	190	191
Bonnydoon ..	Walkamin ..	4.7	4.6	19.5	15.3	50.8	176	176
	Hermitage ..	4.9	5.1	22.1	16.8	46.1	167	167
Hazeldean ..	Walkamin ..	4.2	5.3	19.1	11.5	54.9	179	180
	Hermitage ..	4.3	6.0	22.3	14.5	47.8	166	169
Bolly Golden ..	Walkamin ..	4.3	2.9	15.0	11.3	61.5	193	193
	Hermitage ..	4.5	4.0	18.9	14.8	52.7	180	180
Walkamin means		4.20	3.77	18.37	12.41	56.21	184	184
Hermitage means		4.38	4.46	20.47	14.36	51.30	175	177

Each variety of linseed grown at Hermitage produced larger quantities of palmitic, stearic, oleic and linoleic acids than the same variety grown at Walkamin. Linolenic acid varied from 50.8 to 61.5% (mean 56.21%) at Walkamin and from 46.1 to 58.8% (mean 51.3%) at Hermitage. Each variety grown at Walkamin produced larger quantities of linolenic acid than the same variety grown at Hermitage. Where small district variations in iodine values existed—e.g. in Marine and Newlands varieties—only small differences in fatty acid composition occurred. The mean monthly temperatures at Walkamin during the growing season were from 4.4 to 16.2°F higher than those at Hermitage.

The fact that linolenic acid was produced in higher concentrations in a warmer environment does not agree with the findings of McGregor and Carson 1961. In agreement with these authors, however, linolenic acid was clearly related to iodine value ($r = + 0.97$) and an inverse relationship between linolenic and oleic acids was observed ($r = - 0.91$).

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