# THE MINOR FATTY ACIDS OF RAPESEED OILS

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## INTRODUCTION

Rapid developments in plant breeding have almost eliminated erucic (cis-13-docosenoic) acid from rapeseed oils of either Brassica campestris or B.napus origin (Ackman, 1977a). It is therefore opportune to report on the overall fatty acid compositions of the Canadian licensed "double zero" varieties TOWER and CANDLE, with special attention to minor fatty acids not usually tabulated in compositions.

## MATERIALS AND METHODS

Oils examined were commercially extracted (hexane) and refined by normal procedures (Ward, 1977). Unsaponifiable materials were removed from 500 g of the Tower oil by AOCS procedure Ca-6a-40. Esters were distilled through a Stedman column to concentrate those more volatile than the $C_{18}$ chain length. These were examined by preparative and analytical (open-tubular) gas-liquid chromatography, and ozonolysis in a monophasic reagent system based on $BF_3$/MeOH (Ackman, 1977a; Sebedio and Ackman, 1978a). The Candle oil was studied on a smaller scale (200mg) with esters prepared by transesterification in $BF_3$-MeOH.

## RESULTS AND DISCUSSION

The conventional fatty acids of the current licensed "double zero" varieties TOWER (B. napus) and CANDLE (B. campestris) are given in Table 1. These account for 99.7 and 99.8% respectively of total fatty acids. The order of accuracy is not that indicated by the decimal places but should be ±5% for major (> 10%) components. Similar data for the varieties SPAN, TORCH, and MIDAS has been published elsewhere (Ackman, 1977a).

TABLE 1

IMPORTANT "CONVENTIONAL" FATTY ACIDS OF CANADIAN RAPESEED OILS FROM TWO CONTEMPORARY "DOUBLE-ZERO" VARIETIES IN w/w% OF REFINED OIL

| | Variety | |
|---|---|---|
| Fatty Acid | TOWER | CANDLE |
| 16:0 | 3.88 | 3.82 |
| 18:0 | 1.56 | 1.23 |
| 20:0 | 0.50 | 0.35 |
| 22:0 | 0.28 | 0.20 |
| 24:0 | 0.14 | 0.04 |
| 16:1 | 0.29 | 0.24 |
| 18:1 | 64.02 | 53.50 |
| 20:1 | 1.24 | 1.37 |
| 22:1 | 0.08 | 1.00 |
| 24:1 | 0.09 | 0.25 |
| 16:2ω6 | 0.09 | 0.02 |
| 18:2ω6 | 18.79 | 23.52 |
| 20:2ω6 | 0.05 | 0.11 |
| 16:3ω3 | 0.08 | 0.15 |
| 18:3ω3 | 8.59 | 13.99 |
| 20:3ω3 | 0.01 | - |

TABLE 2

PROPORTIONS OF SOME "MINOR" SHORTER CHAIN FATTY ACIDS OF CANADIAN RAPESEED OILS FROM TWO CONTEMPORARY "DOUBLE-ZERO" VARIETIES IN w/w% OF REFINED OIL

| Fatty acid | Variety | |
|---|---|---|
| | TOWER | CANDLE |
| 14:0 | 0.04 | 0.05 |
| 15:0 | 0.02 | 0.02 |
| 17:0 | 0.05 | 0.04 |
| iso-14:0 | 0.004 | 0.002 |
| anteiso-15:0 | 0.004 | 0.002 |
| 14:1ω9 | 0.007 | 0.010 |
| 14:1ω7 | 0.001 | 0.001 |
| 14:1ω5 | trace | trace |
| 14:2ω6 | 0.004 | 0.002 |
| cis-15:1ω10 | 0.04 | 0.02 |
| trans-15:1ω10 | 0.02 | 0.01 |
| 15:1ω8 | trace | trace |
| 16:1ω9 | 0.06 | 0.03 |
| 16:1ω7 | 0.21 | 0.20 |
| 16:1ω5 | 0.02 | 0.01 |
| 17:1ω8 | 0.06 | 0.03 |

Table 2 gives details of the shorter-chain components. All fit into accepted biochemical patterns for fatty acids except for the cis- and trans-15:1ω10. The provenance of these acids is unknown, although a 15:1ω10 acid is listed as a minor component of spruce (Picea abies) wood (Ekman and Pensar, 1973). Most fatty acids with ethylenic unsaturation in the $\Delta^5$ position are even-chain. The shorter even-chain polyunsaturated fatty acids evidently are derived from chain shortening of the major components 18:2ω6 and 18:3ω3. The shorter even-chain monoethylenic fatty acids show several chain length interchanges (e.g., 18:1ω9 → 16:1ω9 → 14:1ω9, 14:1ω7 ← 16:1ω7 → → 18:1ω7, and 14:1ω5 → 16:1ω5), provided one assumes that the basic origin is through a desaturase acting on the 9th and 10th carbons from the carboxyl group of the corresponding saturated acid.

In methyl esters of both TOWER and CANDLE oils, and indeed in sundry other crude rapeseed oils, we have observed and isolated by $AgNO_3$-TLC the cis-9,cis-12,trans-15- and trans-9,cis-12,cis-15-octadecatrienoic acids previously reported in different refined vegetable oils, (Ackman et al., 1974). With TOWER and CANDLE we have followed these isomers of linolenic acid back to oil extracted in the laboratory from seed. Contrary to the earlier view, these isomers may exist in trace amounts before refining processes are applied. Somewhat less trans-9,cis-12,cis-15 isomer usually accompanies the cis-9,cis-12,trans-15 isomer in all samples examined.

The change in proportion of 22:1ω7 to 22:1ω9 during the reduction in total 22:1 from about 25% to 0.1% has been followed in detail by ozonolysis of isolates with the results shown in Table 3. As the total 22:1 diminishes the proportion of 22:1ω7 increases. Monoethylenic isomers in other chain lengths are detailed elsewhere (Sebedio and Ackman, 1978b).

The important fatty acids from a thorough investigation of several of the newer low-erucic Canadian varieties of rapeseed oil (SPAN, TORCH, MIDAS, TOWER), and of two prospective yellow seed coat B. campestris varieties, have appeared elsewhere (Ackman, 1977b). Details of the analytical technology establishing the minor components will also appear

elsewhere (Sebedio and Ackman, 1978b).

TABLE 3

PROPORTIONS OF 22:0, 22:1ω9 AND 22:1ω7 IN VARIOUS RAPESEED OILS

| | "High-erucic" | | SPAN | | TOWER | | CANDLE | |
|---|---|---|---|---|---|---|---|---|
| | Isomer % | % in oil | Isomer % | % in oil | Isomer % | % in oil | Isomer % | % in oil |
| 22:0 | - | 0.4 | - | 0.2 | - | 0.2 | - | 0.2 |
| 22:1ω9 | 99.1 | 23 | 98.2 | 2.7 | 97.7 | 0.1 | 98.9 | 1.0 |
| 22:1ω7 | 0.9 | | 1.8 | | 2.3 | | 1.1 | |

The objectives of the genetic manipulation of rapeseed have included lowering of erucic acid content in the oil, reduction of glucosinolates in the seed, and conversion to yellow seed coat, as well as introduction of other characteristics to promote rapid growth, yield of seed, and improved oil and protein contents (Downey, 1976). The rapeseed plant shows remarkable tenacity in producing the same minor fatty acids despite these pressures. Other oil constituents such as sterols and tocopherols also are very little affected (Ackman, 1977a; Kovacs et al., 1978). The low-erucic acid rapeseed oils are, however, a new type of edible oil, sufficiently different from traditional rapeseed oils, and from the other edible oils, to warrant serious consideration being given to a new name.

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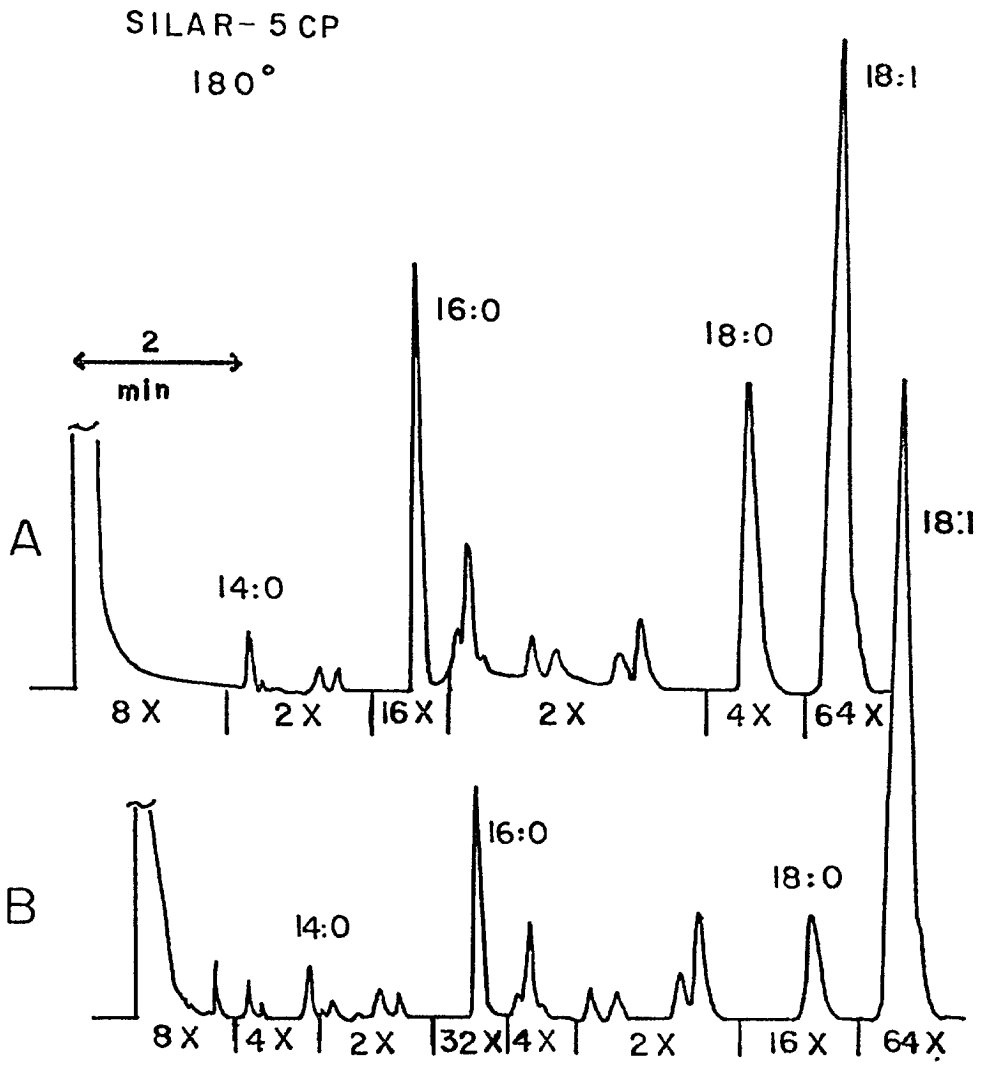


Figure 1. Parts of GLC analyses of shorter-chain methyl esters of total fatty acids of high (ca. 25%) erucic acid (B) and low-erucic acid (A) rapeseed oils, indicating overall similarity in proportions of Table 1 minor components (note attenuation changes).