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The sterol fraction of rapeseed oils in relation to variety

by Goffredo Lotti, and Serfio Baragli

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The Sterol Fraction of Rapeseed Oils in Relation to Variety

by Goffredo Lotti, Sergio Baragli

Summary

The composition of the sterol fraction of the unsaponifiable of seed oils of a series of varieties of rapeseed grown in the same soil and climate conditions was examined by TLC-GLC.

In all the oils examined, the results obtained, over and above the basic sterols (β- sitosterol, campesterol and brassicasterol),indicated the presence of small quantities of Δ^5-avanasterol, Δ^7-stigmastenol, cholesterol and traces of stigmasterol. From the quantitative viewpoint, the composition of the sterol fraction appears to be considerably influenced by varietal factors.

Sterol composition of the unsaponifiables from rapeseed oils of varieties grown in the same pedoclimatic environment was determined by TLC-GLC. The obtained results have shown in all oils the presence of fundamental sterols (β-sitosterol, campesterol and brassicasterol) and minor quantities of Δ^5-avenasterol, Δ^7-stigmastenol, cholesterol and traces of stigmasterol. From a quantitative point of view sterol composition of rapeseed oils appears markedly affected by varietal factors.

Studies on the effects of varietal factors on the analytical characteristics and on the acid composition of oils have developed remarkably in recent years, and have been the subject matter of numerous researchers, including some of our own. We mention only a few investigations on the most common edible oils and more specifically those on the oils of almonds (19), olives (3,20), cherries (22), safflower (18), maize (13, 21), rice (14) and sunflower (15). Recently we also turned our attention to the oils of rapeseed varieties grown in Italy (4, 16), in view of the renewed interest in the growing of rape as an oil-bearing plant as well as in the nutritional problems of its oil, due to its high erucic acid content. The composition and the characteristics of the oils of the various rape varieties have been fully studied in the countries where the consumption of this oil is highest (Canada, France, Sweden, Poland, etc.), as may be seen from the literature (1, 2, 7, 25, 28), and in recent years varieties having a very low content of or indeed completely lacking in erucic acid have been introduced.

Therefore while knowledge on the effect which the variety may have on the fatty acid composition of plant oils in general and of rapeseed oils in particular is very broad, on the other hand contributions aimed at testing the possible effect of the variety on the components of the unsaponifiable fraction and, especially on sterols, the spectrum of which is a common characteristic of the various plant species, appear to be very meager.

It should also be borne in mind that these studies need to be conducted on crude oils and not on commercial oils, because it is known that refining operations can lead to alterations in the composition of the substances present in the unsaponifiable fraction.

As regards rapeseed oil, the literature contains numerous researches on the sterol fraction (6, 8, 9, 10, 11, 17, 24, 26), which (on the whole)

indicate that the basic sterols of rapeseed oil are ß-sitosterol, campesterol and brassicasterol in that order, accompanied by lesser quantities of cholesterol, Δ^5-avenasterol and Δ^7-stigmastenol (12), while stigmasterol is practically absent.

It must be pointed out that in general the rapeseed oils examined are commercial ones and that for the crude oils the variety is hardly ever mentioned (5).

Materials and Methods

The rapeseed of the thirteen varieties examined were kindly supplied to us by the Institute of Agronomy and Herbacous crops of the University of Pisa and they refer to the 1973 crop.

These were the mature seeds of four varieties adapted to Italy, three varieties from Germany, three from France and three from Sweden. All the varieties had been grown on land belonging to the Tombolo (Pisa) Experimental Centre under practically identical growing and soil and climate conditions.

The oil was extracted in Soxhlet with petroleum ether (p.e. 40°C) from seeds previously dried in an oven at 60°C and finely ground. The unsaponifiable substances were separated from the oils in accordance with official methods of analysis of fatty substances, using ethyl ether, and the composition of the sterol fraction was determined by TLC-GLC according to the method reported in N.G.D. (23). The separation of the various bands on a thin layer of silica gel was carried out with a 95:5 (v/v) benzol-acetone mixture, while the trimethylsilylethers were prepared with the pyridine-hexamethyldisilazane-trimethylchlorosilane 9:3:1 (v/v) reagent.

The gaschromatography was carried out with "Perkin-Elmer 900" apparatus, with flame ionization detectors and column packed with OV 17 (poly-methylphenylsiloxane) at 1.5% on Varoport 100-120 mesh.

The operating conditions of the apparatus were: temperature of the column 264°C; temperature of the injector 320°C; temperature of the detector 290°C; flux of carrier gas (nitrogen) 32 ml/min.

The sterols present were identified by measuring the retention times for ß-sitosterol (12), confirmed by the addition of standard samples and determined quantitatively through triangulation.

Results and Discussion

Shown in Table 1 are the findings on the percentage composition of the sterol fraction of the rapeseed oils of various varieties, together with the level of unsaponifiable substances in the oils and their erucic acid content, determined in a previous work (4), while Figure 1 gives, as an example, the gaschromatograms relating to the sterols of Matador and Mayor varieties.

From the data of the table it may be seen that the level of unsaponifiable substances in the different oils is within a very limited range, with an average value of 1.00%.

As regards the sterol composition of the unsaponifiable, it is seen first of all that, from the qualitative viewpoint, the oils of all varieties always contain the same sterols and more specifically ß-sitosterol, campesterol, brassicasterol, cholesterol, Δ^5-avenasterol and Δ^7-stigmastenol, as well as traces of stigmasterol. The Δ^5-avenasterol was identified by the relative retention time equal to 1.12 and the Δ^7-stigmastenol by its retention time of 1.19.

The qualitative composition of the sterols agrees with what was reported in the literature, in particular by Itoh et al. (12) for rapeseed oil. The Δ^5-avenasterol has also recently been found in the oils of olives, safflower and sunflowers (27) and therefore is to be considered a normal component of the oils, in small quantities, even if some oils (coconut, castor-oil, linseed oil) contain very high quantities of it (24).

The Δ^7-stigmastenol may also be considered common in all plant oils, in quantities of 1-6%, with remarkably high quantities (up to 20%) being found in some oils, like those of the sunflower and safflower. Less common in oils and anyway generally present only in traces is cholesterol.

From the quantitative viewpoint, particularly important is the considerable diversity of the sterol composition of the oils of the different varieties of rape examined, which indicates a clear influence of varietal factors on the composition of this fraction of the unsaponifiable.

The sterol present in the highest quantity is ß-sitosterol which ranges from 49.01 in the SV 67 to 59.39% in the Ramses, followed by campesterol, which rises from 26.50 in the Sarepta to 39.09% in the Sinera and by the brassicasterol, which varies from 7.86 in the Mayor to 16.35% in the Matador.

The other sterols appear in considerably lesser quantities. The Δ^5-avenasterol in fact ranges from a minimum of 1.07% in the Sinera and Matador varieties to a maximum of 4.02% in the Erusine, while the Δ^7-stigmastenol, present in quantities of 0.02% in the Torrazzo and Ramses varieties, reaches a maximum value of 0.90% in the Sarepta. Finally, cholesterol ranges in the various oils between 0.12 and 0.90%, while stigmasterol always appears in traces. Overall, the quantitative composition falls within the order of magnitude of the known data for rapeseed oils; in the varieties examined by us, only a higher cholesterol content and a lower Δ^7-stigmastenol content are observed.

Since the varieties examined have very different erucic acid contents, we wanted to determine whether this content was in relation to the individual sterols. The ratios between erucic acid and the sterols have demonstrated that no relationship exists, which in the last analysis means that there is no connection between the acid composition and the sterol composition of the unsaponifiable fraction of the oil.

Between the various sterols, the ratio between ß-sitosterol and campesterol varies greatly, ranging between 1.28 and 2.16, as does the ratio between campesterol and the rapeseed sterol -- brassicasterol -- which ranges from 1.8 to 4.9.

Finally, we note that, from the viewpoint of a mixing of the seed oils, an addition of rapeseed oil leads to a sharp increase in the level of brassicasterol, which is practically absent in the oils not deriving from seeds of Crucifers. In particular, its addition to olive oil would also greatly increase the campesterol content, while it markedly reduces that of ß-sitosterol.

In conclusion, we can say that in the oils of various varieties of rapeseed, grown in the same soil and climate conditions, the varietal factors have a consideralbe effect, from the quantitative viewpoint, not only on the acid composition, but also on the composition of the sterol fraction of the unsaponifiable.

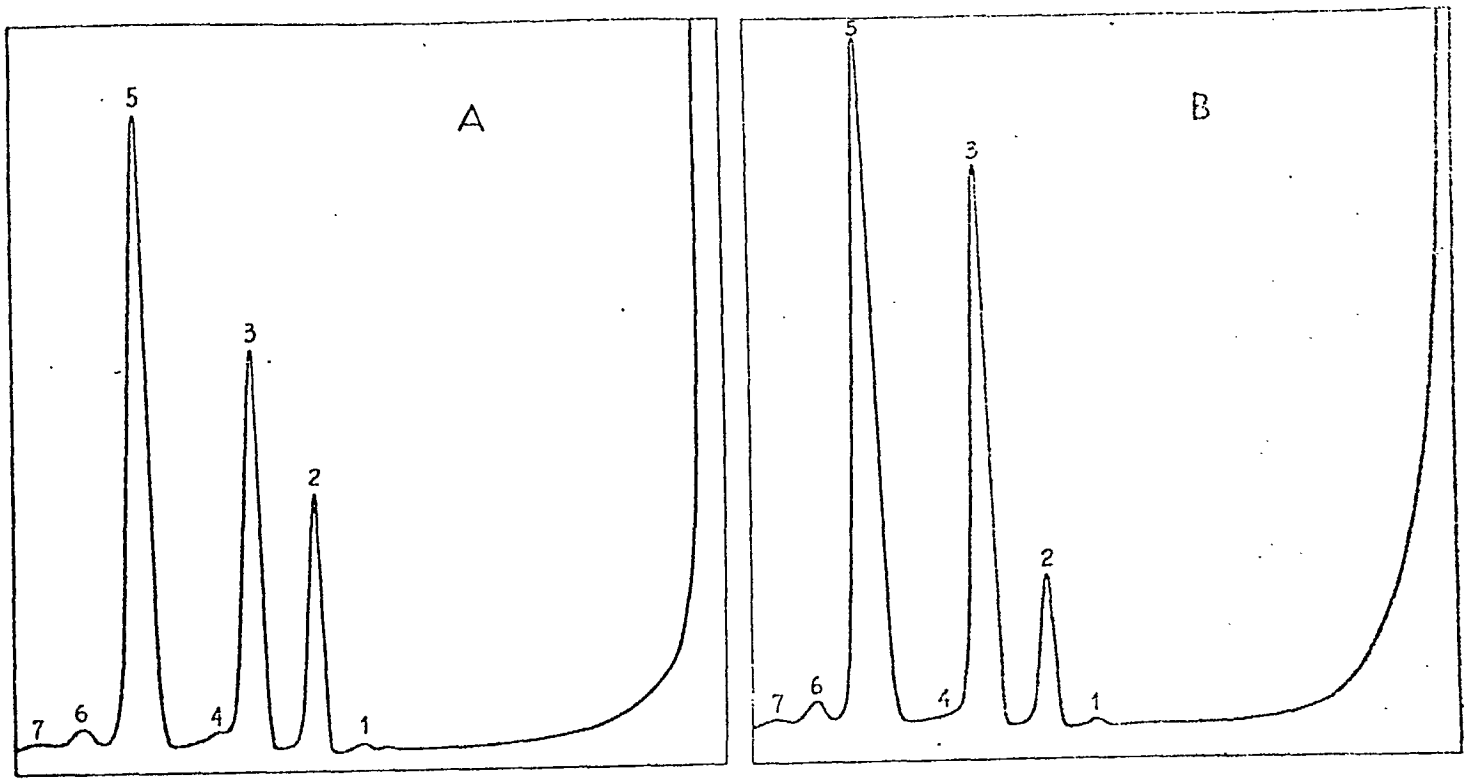

Fig. 1. Sterol composition of rapeseed oils of the Matador (A) and Mayor (B) varieties.

1) cholesterol 2) brassicasterol 3) campesterol 4) stigmasterol 5) ß-sitosterol 6) Δ^5-avenasterol 7) Δ^7-stigmasterol

Table 1

Percentage Composition of the Sterol Fraction of a Series of Rapeseed Oils

Cultivar	Origin	Unsaponifiable %	Erucic Acid %	Sterol composition of the unsaponifiable							
				Cholesterol	Brassicasterol	Campesterol	Stigmasterol	β-sitosterol	Δ^5-avenasterol	Δ^7-stigmastenol	β-sitosterol / campesterol
Leonessa	Italy	1,01	47,4	0,15	11,95	32,42	tr.	51,85	3,43	0,18	1,77
Matador	Italy	0,96	46,6	0,22	16,35	29,10	tr.	53,05	1,07	0,19	1,82
Olimpiade	Italy	1,06	47,2	0,23	10,62	36,95	tr.	50,36	1,65	0,15	1,36
Torrazzo	Italy	0,99	48,1	0,29	13,71	30,89	tr.	53,41	1,39	0,02	1,73
Erusine	Germany	1,11	9,1	0,28	8,15	31,33	tr.	55,59	4,02	0,58	1,77
Sinera	Germany	0,98	3,3	0,73	8,70	39,09	tr.	50,05	1,07	0,33	1,28
Synra	Germany	0,92	50,3	0,86	8.87	35,14	tr.	53.29	1,93	0,08	1,51
Ramses	France	1,03	47,5	0,90	10,49	27,45	tr.	59,39	1,84	0,02	2,16
Sarepta	France	1,04	49,7	0,12	12.70	26,50	tr.	55,76	2,86	0,80	2,14
Mayor	France	0,90	45,4	0,26	7,86	33,51	tr.	51,39	1,70	0,26	1,33
SV - Sinus	Sweden	0,97	12,5	0,15	15,78	32,49	tr.	49,89	1,83	0,18	1,53
SV 71/15010	Sweden	1,10	12,4	0,70	14,30	34,25	tr.	49,29	1,40	0,14	1,43
SV 67/8144	Sweden	1,02	23,6	0,23	15,65	33,18	tr.	49,61	2,27	0,20	1,47
Average Value		1,00	—	0,39	11,88	32,87	tr.	52,53	2,04	0,24	—
Retention Time				0,62	0,71	0,82	0,89	1,00	1,12	1,19	—

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11) Composition of the sterol fraction of plant oils determined by gaschromatography.