NATURAL PRODUCTS CHEMISTRY OF RAPESEED

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The classical treatise "Rapeseed", edited by Appelqvist and Ohlson (1), as well as the Proceedings of the past four International Rapeseed Conferences contain much information on the constituents of rapeseed. Therefore, the present review is limited to a survey of the literature published in the last four years.

GROSS COMPOSITION

The new varieties of rapeseed (2, 3) show a gross composition similar to that of the conventional ones (1). This is also reflected in the composition of the corresponding meals (4).

The proportions of lipids, carbohydrates and proteins in rapeseed change during development of the seed, as shown in the following figure.

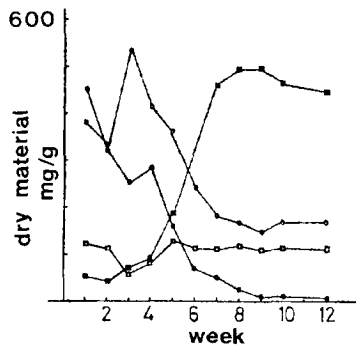

Fig. 1: Contents of lipids ●—●—● carbohydrates ■—■—■ and proteins □—□—□ during development of rapeseed (B. napus, Panter) (5).

LIPIDS

The composition of lipids in rapeseed has been the subject of a comprehensive review published recently (6).

Acyl lipids. The proportions of various lipid classes in developing rapeseed have been reported (5). During maturation, the content of neutral lipids (storage lipids), increases whereas that of ionic and other polar lipids (structural lipids) declines (5).

Stereospecific analyses of the triacylglycerols of conventional and new varieties of rapeseed have been reported (7). The fatty acid composition of the triacylglycerols in some new varieties of rapeseed has been determined (8-11); a few typical results are given in the following table (Table 1).

The fatty acid composition of various classes of neutral (12, 13) as well as of ionic and other polar lipids (12) has been determined.

Steroids and other isoprenoid compounds. The sterols in the non-saponifiable fraction from the seeds of conventional and new varieties of rape have been characterized (14-18). The composition of the sterols in the

TABLE 1

FATTY ACID COMPOSITION OF THE SEED OILS FROM NEW VARIETIES OF RAPE (8-11)

Chain length: Number of double bonds	Brassica campestris		Brassica napus	
	Span	Torch	Midas	Tower
12:0	0.01	0.01	0.01	0.01
14:0	0.04	0.04	0.05	0.05
15:0	0.01	0.01	0.02	0.01
15:1	0.01	0.01	0.01	0.02
16:0	3.46	3.18	3.84	3.88
16:1	0.28	0.22	0.29	0.29
16:2 w 6	0.03	0.03	0.06	0.09
16:3 w 3	0.09	0.12	0.10	0.08
17:0	0.04	0.04	0.04	0.04
17:1 w 8	0.06	0.05	0.05	0.06
18:0	1.32	1.45	1.69	1.56
18:1	57.24	65.74	64.33	64.02
18:2 w 6	21.64	18.24	18.98	18.79
18:3 w 3	8.96	9.46	8.11	8.59
19:0	0.02	0.02	0.01	0.02
19:1 w 10	0.02	0.02	0.02	0.02
20:0	0.38	0.41	0.55	0.50
20:1	2.63	1.14	1.16	1.24
20:2 w 6	0.14	0.07	0.04	0.05
20:3 w 3	0.02	0.01	0.01	0.01
21:0	0.01	0.01	0.01	0.01
22:0	0.23	0.18	0.33	0.28
22:1	2.74	0.22	0.02	0.08
24:0	0.13	0.11	0.13	0.14
24:1	0.30	0.15	0.13	0.09

seeds of four varieties of rape is given in the following table (Table 2).

TABLE 2

STEROL CONTENTS OF SOME RAPESEED OILS (16-18)

Variety	% in oil	Relative %				
		Brassica-sterol	Chole-sterol	Campe-sterol	Stigma-sterol	Sito-sterol	Others
Canbra	0.53	7.4	-	35.5	-	57.1	-
Primor	0.79	8.0	0.8	40.5	-	50.7	-
Erglu		10.3	0.5	42.6	-	44.6	2.0
Lesira		7.2	0.3	38.7	-	52.1	0.9

It should be noted that brassicasterol is present in many oilseeds, but not in as high proportions as in rapeseed (14).

The triterpene alcohols isolated from the lipids of rapeseed are found to consist of β-amyrin, cycloartenol and 24-methylcycloartanol in addition to about ten similar compounds which were not identified (15).

The tocopherols in rapeseed have been characterized and quantitatively de-

termined (19, 20).

Surface waxes. The epicuticular lipids of rapeseed, which during processing will enter the oil, have been found to contain hydrocarbons, wax esters, aldehydes, prim. and sec. alcohols, and hydroxyketones (21).

The hydrocarbon fraction on the seed surface of several cultivars of rape have been analyzed and found to be characteristic of the respective variety (21). In this context, detailed studies on the chemistry and ultrastructure of the "waxes" occurring on the leaf of rape are of great interest (22, 23).

CARBOHYDRATES AND GLUCOSINOLATES

A comprehensive review on the carbohydrates of rapeseed has appeared recently (24).

About one-half of the polysaccharides in dehulled oil-free rapeseed meal has been found to be composed of arabinogalactan, arabinan, amyloid and cellulosic residue, whereas the other half consists of pectin (24). The amyloid (25), the pectin (26) as well as the lignins (27) in rapeseed hulls have been thoroughly characterized.

The carbohydrates of low molecular weights have been determined in six cultivars of rapeseed (28); the results are shown in the following table (Table 3).

TABLE 3

LOW-MOLECULAR WEIGHT CARBOHYDRATES IN RAPESEED* (28)

Cultivar	Fructose	Glucose	Sucrose	Galactinol	Digalactosylglycerol	Raffinose	Stachyose
Victor	0.10	0.10	6.60	0.06	0.09	0.31	1.43
Sinus	0.17	0.17	7.57	0.16	0.07	0.30	2.29
Gulle	0.27	0.22	6.94	0.24	0.10	0.29	3.04
Bronowski type	0.17	0.24	6.63	0.11	0.11	0.33	2.47
Duro	0.51	0.40	7.44	0.10	0.10	0.31	2.39
Bele	0.24	0.32	6.77	0.11	0.09	0.34	2.43

*Given as % of dry defatted rapeseed meal.

In recent years, the chemistry and biochemistry of the glucosinolates, the most characteristic constituents of rape and other Cruciferae, have been reviewed (29, 30). Several new methods have been proposed for the assay of total glucosinolates (31) and for the quantitative determination of the individual compounds (32-34). NMR Spectroscopy and mass spectrometry have been employed for the identification of glucosinolates and related compounds (35). Among the sulfur-containing decomposition products of glucosinolates, several isothiocyanates and oxazolidinethiones have been identified (36, 37). In addition, cyano compounds have been found in the seeds and leaves of rape (38) as well as rapeseed oil (36).

PROTEINS AND AMINO ACIDS

Studies on the seed proteins of Cruciferae species and their taxonomic va-

riations are well documented in a recent review (39).

The major reserve proteins of rapeseed, the globulins having a sedimentation coefficient of about 12 s, have been isolated from several Brassica species and extensively characterized (40-42). In addition, several basic proteins having a sedimentation coefficient of 1.7 s have been isolated from rapeseed and some of their properties have been studied (43, 44). Secondary structures of both 12 s and 1.7 s proteins have been studied by circular-dichroism measurements (45).

Solubility of rapeseed proteins in aqueous solutions (46-49), structural changes of these proteins during extraction with various solvents (50), and their behavior during precipitation from alkaline extracts (48, 49) have been reported. Based on these studies, methods have been developed for the preparation of protein isolates from rapeseed in high yield and purity (48, 51). As examples, the gross composition of two protein isolates obtained from each of two new varieties of rapeseed, B. napus, Lesira and Erglu, is shown in the following table (Table 4); the composition of the meals is given for comparison.

TABLE 4

COMPOSITION OF RAPESEED MEALS AND PROTEIN ISOLATES*(52)

	Erglu			Lesira		
	Meal	Isolate I	Isolate II	Meal	Isolate I	Isolate II
Oil (%)	0.9	0.0	0.0	0.8	0.0	0.0
Protein (%)	41.3	92.9	98.6	39.4	99.6	99.3
Ash (%)	8.26	0.78	0.33	7.28	0.04	0.10
Fiber (%)	13.11	0.07	0.02	17.86	0.00	0.00
Nitrogen-free extract (%)	36.43	6.25	1.05	34.66	0.36	0.60
Oxazolidine-thione, mg/g	0.65	0.00	0.00	13.50	0.00	0.00
Isothiocyanates, mg/g	0.20	0.00	0.00	3.20	0.00	0.00

*Values are given on a dry weight basis.

The amino acid composition of these protein isolates and of the rapeseed meals from which they were prepared, is given in the following table (Table 5).

Little is known so far on the composition and structure of proteins in protein concentrates and protein isolates obtained from rapeseed. Recent work in the authors' laboratory (53) and elsewhere (54) has revealed that the structure of the native proteins of rapeseed is considerably altered during the extraction and isoelectric precipitation. It has also been found that an array of acidic constituents of rapeseed, such as phytic acid, ribonucleic acids, acidic carbohydrates and acidic polyphenols interact with the proteins of rapeseed during their isolation. Thus, all of these substances can be found in rapeseed protein isolates (53, 55). It seems that these interactions are not only limited to rapeseed proteins, but they also occur during the isolation of proteins from most of the other oilseeds (55, 56).

TABLE 5

AMINO ACID COMPOSITION OF RAPESEED MEALS AND PROTEIN ISOLATES* (52)

Amino acid	Erglu Meal	Erglu Isolate I	Erglu Isolate II	Lesira Meal	Lesira Isolate I	Lesira Isolate II
Lysine	6.32	5.97	4.73	6.49	5.42	3.39
Histidine	3.38	3.36	3.22	3.28	3.18	3.00
Arginine	6.62	7.45	7.22	6.58	6.04	7.38
Threonine	4.76	4.69	4.06	4.52	4.64	4.05
Valine	4.76	5.01	4.77	5.31	5.04	4.65
Methionine	1.50	1.91	2.26	1.80	1.80	1.96
Total sulphur amino acids	3.27	4.11	3.86	2.99	4.22	3.06
Isoleucine	4.05	4.67	4.37	4.00	4.43	4.41
Leucine	7.63	8.56	8.30	7.44	8.81	8.75
Phenylalanine	4.67	5.27	5.85	4.80	5.22	5.36

*Values are given in g/16 g N.

OTHER ORGANIC COMPOUNDS

It appears that the nucleic acids in rapeseed have not been studied, though their presence in fractions of the seed proteins have been reported (41, 53, 55).

As in all cereals, oilseeds and legumes, phytic acid and phytates are found in rapeseed (57).

The phenolic constituents of rapeseed include tannins (58) as well as sinapic acid and related compounds (27, 59), polyphenols and lignins (27).

Reference is made to a review on the volatile compounds that have been isolated from various Cruciferae species (60).

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