

CHEMISTRY**Summary of presentations in this section
and review of recent years progress****Hilmer Sørensen**

Chemistry Department,
Royal Veterinary and Agricultural University,
40, Thorvaldsensvej, DK-1871 Frederiksberg C, Denmark.

The subjects covered in the chemistry section reflect the quantitative and qualitative important groups of crucifer or rapeseed constituents. The research and development are moving forward on a broad front, in some branches rapidly, but in several cases it is disappointing to see the slow progress in relation to the effort and resources used. Although it can be difficult in some cases to draw borderlines, the subjects presented can with advantages be divided into major areas:

- (1) **Proteins - (2) Oil - (3) Carbohydrates**
- (4) **Native low molecular weight physiological active components or transformation products thereof, enzyme and metabolism studies**
- (5) **Quality of rapeseed products as influenced by the rapeseed constituents (1-4)**
- (6) **Analytical methods and techniques required for studies of the subjects (1-5).**

The research contributions to the chemistry section comprises 55 papers with representation from 16 countries: Austria, Belgium, Canada, Czechoslovakia, Denmark, Finland, France, Germany, India, Italy, Norway, Poland, P.R. China, Sweden, United Kingdom, USSR. Canada and France contributed each with about 20% of the presentations and each of the other countries contributed with 2-7% of the papers.

Oil and proteins are the primary or quantitatively important rapeseed products accounting for 40-46% and 20-28%, respectively, of the rapeseed dry matter, followed quantitatively by approximately 20% carbohydrates of which starch only account for 2-3%. Relatively few contributions cover exclusively these subjects.

Important contributions have, however, been devoted proteins, the amino acid composition and properties of rapeseed protein fractions and possibilities of influencing

the sizes of the different fractions by breeding. A very interesting paper presents information on **oleosins**, relatively low molecular weight amphipatic rapeseed proteins.

Rapeseed proteinase inhibitors of protein type are also considered in two contributions which call for attention.

Dolichols, a homologous series of isoprenoid alcohols, are unsaturated compounds containing 14-24 isoprene units. These compounds are considered in relation to biosynthesis of glycoproteins various uses in biological studies and as constituents of rapeseed oil. Properties of canola oil and formation of sterol oxides in products fried in canola oil have been evaluated as have the potentiality for various uses of sulfonated oil. Several papers consider the well known problems caused by chlorophyll and various products from especially degradation of glucosinolates during rapeseed processing.

The carbohydrate content of yellow-seeded canola is, in an interesting paper, compared to the content of these compounds in brown-seeded varieties. The subject, comprising dietary fibres in rapeseed, is considered as a special important research area in relation to the quality and nutritive value of rapeseed/rapeseed meal. This is also stated in some few of other papers both in this and other sections.

Native low molecular weight rapeseed constituents and/or transformation products thereof are often physiological active compounds. The contributions to the subject at this meeting reveal, that the compounds considered to be most important in this connection are: lipids, amino acids, phenolics comprising tannin and aromatic choline esters, and especially glucosinolates and products thereof, which affect the rapeseed quality. 4-Hydroxyglucobrassicin is described as a compound, which needs attention owing to its relative high concentration in double low rapeseed and effects on the quality of rape products. This very unstable glucosinolate has been isolated in appreciable amount, and both the intact compound and degradation products thereof have now been studied in animal trials in relation to unsolved problems with rapeseed quality. Toxins produced as result of fungal blackleg disease are considered in an other encouraging work, which also gives various reasons for additional focus on indolylglucosinolates and products thereof. In this connection research described on synthetic natural and artificial glucosinolates are an area of great interest.

Metabolism of glucosinolates is an area of major interest. Focus has been placed on specific enzymes involved in biosynthesis of glucosinolates, possible metabolic blocks and the formation of N-hydroxyamino acids and aldoximes. In two very interesting papers isolation and studies of the enzymes catalysing the last two steps in the glucosinolate

biosynthesis have been presented. Brassica napus seedlings have been used for isolation of the enzymes UDP-glucose: Thio-hydroximate glucosyltransferase and Phosphoadenosyl sulfate: Desulfoglucosinolate sulfotransferase. Antibodies are produced against the sulfotransferase, and for this enzyme studies on the mRNA level have been performed. It is thus the most fundamental and complete investigations performed up to now on enzymes involved in the glucosinolate biosynthesis. Myrosinases, their characterization, immunochemical and other properties are treated carefully in papers on this subject. Also fatty acyl-CoA thioesterase has been studied and in this case with use of capillary electrophoresis, which seems to be a new promising analytical technique.

The quality of rapeseed products varies as a result of several factors (vide supra). Glucosinolates and products thereof as well as dietary fibres are especially important in relation to optimal utilization of the rapeseed protein, and for the oil other compounds need attention.

Natural oxidants from rapeseed comprise various **phenolics** as described in one of the contributions. In an other paper tannin and methods of analyses for this heterogenous group of compounds are the subject for a critical evaluation. Sinapine and other aromatic choline esters are among the quantitatively dominating phenolics in rapeseed, and methods of analysis for sinapine are among the subjects considered. S-Methylcysteine sulfoxide is an other subject for a paper on analytical methods, as are determination of amino acids using the OPA-HPLC technique.

Analytical methods and techniques are the subject several papers are concerned with, including more or less well known methods of glucosinolate determinations. NIR has been described in several papers both as a method for determination of fatty acid, glucosinolates and other compounds. Determination of sulfur has been used as a measure of total glucosinolates. It is described in papers presented, that both X-ray fluorescence (X-RF) and determination by elementary analysis can be used for the sulfur/glucosinolate determination. The technique based on elementary analysis allows also simultaneous determination of carbon and nitrogen, where the N-values are used as a measure of protein. In some few papers, methods of analysis for glucosinolate degradation products (aglucones) have been considered, including a new approach to colorimetric determination of volatile isothiocyanates. The methods of total glucosinolate analysis based on glucose release have been described as simple and fast methods. The methods presented comprise an improved technique using glucose-test strips, a new technique based on FIA analysis, and a new application using myrosinase immobilization by covalent bonding of the

enzymes to an inert solid matrix. Immuno-enzymatic glucosinolate determination based on use of antibodies against glucosinolates is also presented in a paper. Most of the papers dealing with determination of glucosinolates are, however, devoted the techniques based on HPLC. Among these, the EEC method is presented, as are the possibilities of determination of intact glucosinolates by HPLC-Frit-FAB technique allowing simultaneous glucosinolate identification. Finally, among the huge number of methods is a new and simple technique for analyses of individual anions, carboxylates, intact- and desulfoglucosinolates based on HPCE-CTAB micellar electrokinetic chromatography.

In conclusion:

Rapeseed oil is of high quality with a high content of nutritive valuable unsaturated fatty acids. Change of the oil quality as a result of storage/rancidity, processing/frying, e.g. owing to products formed as a result of these processes deserve further attention.

Rapeseed proteins have a well balanced amino acid composition resulting in possibilities of a high nutritive value if antinutritional compounds are avoided in the products. Further improvements will be of value and seems also to be possible with respect both to amount, amino acid composition, digestibility, chemical properties, functional properties and could be on a par with those reported ongoing investigations of oleosins.

Carbohydrates in rapeseed are quantitatively dominated by dietary fibres. This is a heterogenous group of compounds where very much research work needs to be done with respect to structure and properties of the various glycans and other compounds which make up dietary fibres.

The low molecular weight rapeseed constituents and transformation products of these compounds are an area where much is known at present and appreciable progresses have been obtained during the recent years. Much need still to be done with respect to especially phenolics, "tannin", glucosinolates and products formed therefrom. The heterogenous group "tannin" is nearly a "black box" with respect to our knowledge concerning structures and properties of the real harmful and antinutritional compounds. Important information has now been presented on the enzymes catalyzing the last two steps of the glucosinolate biosynthesis, and on the various forms of myrosinases. More need to be done with respect to the various biosynthetic steps from the amino acid precursors to the last two steps in the glucosinolate biosynthesis as well as with respect to the products formed from glucosinolates, we have an urgent need for more information.

Analytical methods and techniques have in the recent years obtained a very high level. A pressing problem is, however, to learn the users of the methods to select the right methods and techniques in agreement with their need. Elementary analyses, X-RF, NIR, FIA and various colorimetric methods can be simple and sufficient for many purposes. In relation to research studies and control of antinutritional/toxic compounds and quality connected to these compounds, we need to have determination of the individual compounds. GLC and HPLC have the potential and are in many cases developed as suitable techniques to these purposes. With the new promising techniques based on capillary electrophoresis (HPCE), many additional progresses will be seen in the future for various low molecular weight compounds and polymers, proteins, enzymes and carbohydrates.