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Note

Rapid gas chromatographic determination of volatile degradation products of glucosinolates in rapeseed oil

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Rapeseed, similarly to other *Brassicaceae* seeds and plants, contains up to 5% of sulphur heterocyclic compounds, called glucosinolates, which are partially decomposed during rapeseed processing or storage. The most important degradation products are isothiocyanates, vinyloxazolidinethione and nitriles, which contaminate crude rapeseed oils, impairing their refining, hydrogenation, transesterification, etc.

Volatile degradation products of glucosinolates are usualy determined by gas chromatography with flame ionization detection (FID) and the international standard method[1] is based on this principle. Compared with the content in seeds and extraction meals, the content of glucosinolate degradation products in oils is one (in crude oils) or several (in refined or hydrogenated oils) orders of magnitude lower so that an isolation and concentration step is necessary if FID is being used. Therefore, we have applied more selective and more sensitive detectors for this determination.

EXPERIMENTAL

Material

Plant-scale-produced crude and refined rapeseed oils were analysed. Butyl isothiocyanate, used as an internal standard, was synthesized according to Franzke *et al.*[2].

Apparatus

A Hewlett-Packard Model 5880 A apparatus equipped with flame photometric and nitrogen–phosphorus-specific detectors and a glass column (8 ft. × 1/16 in. I.D.) packed with 10% Carbowax 20M on Chromaton N AW DMCS (particle size 0.125–0.160 mm) was used. The carrier gas was nitrogen at a flow-rate of 30 ml min^{-1}. Linear programming from 100 to 200°C at 6°C min^{-1} [flame photometric detection (FDP)] or a constant temperature of 150°C [nitrogen–phosphorus detection (NPD)] was applied. The injection temperature was 220°C in both instances.

Procedure

About 3 g of rapeseed oil were weighed to the nearest 0.01 g, dissolved in 5 ml of

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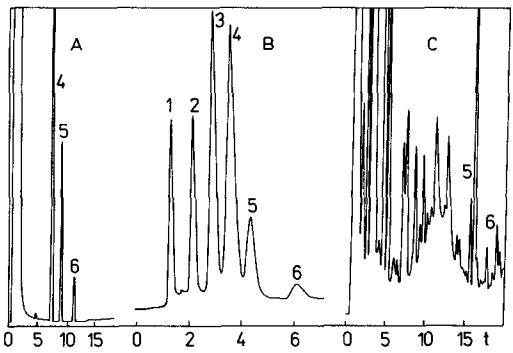

Fig. 1. Separation of volatile glucosinolate degradation products in rapeseed oil. Conditions as described in the text (FPD, NPD). FID: conditions according to ISO[1]. Injection temperatures 220°C in all instances. t = retention time (min). Detection: (A) FPD; (B) NPD; (C) FID. Degradation products: 1 = 1-cyanopropane; 2 = 1-cyano-3-butene; 3 = 1-cyano-4-pentene; 4 = butyl isothiocyanate; 5 = 3-butenyl isothiocyanate; 6 = 4-pentenyl isothiocyanate.

heptane, 1 ml of a standard heptane solution containing 10 μg of butyl isothiocyanate and 10 μg of 1-cyanopropane was added and 6 μl of the mixture were injected for the analysis. The column performance remains constant for 60 injections, and the column should then be replaced, if the sample is being injected directly into the column. The column performance may be prolonged if the sample is injected into the injection port, and the non-volatiles are removed after 60 injections.

RESULTS AND DISCUSSION

Well resolved peaks of isothiocyanates were obtained using FPD and well resolved peaks of both isothiocyanates and nitriles were obtained with NPD (Fig. 1). FPD gave results similar to those reported by Daun and Hougen[3], but the content of less volatile sulphur compounds was lower than those reported. Relative retention times of the most important volatile rapeseed glucosinolate degradation products are given in Table I.

The average contents of nitriles and isothiocyanates were 10–18 and 6–9 mg kg^{-1} in crude oils and 0.01–0.10 and 0.04–0.15 mg kg^{-1} in refined oils, respectively. The

TABLE I

RETENTION DATA AND SENSITIVITIES OF THE GAS CHROMATOGRAPHIC DETERMINATION OF VOLATILE GLUCOSINOLATE DEGRADATION PRODUCTS USING FID

Analysed substance	*Relative retention time*[a]	*Limit of determination (mg kg^{-1})*	*Limit of identification (mg kg^{-1})*
1-Cyano-3-butene	0.634	0.04	0.00138
1-Cyano-4-pentene	0.837	0.03	0.00046
3-Butenyl isothiocyanate	1.186	0.03	0.00034
4-Pentenyl isothiocyanate	1.464	0.01	0.00009

[a] Butyl isothiocyanate = 1.00.

TABLE II

REPEATABILITIES OF THE DETERMINATION OF VOLATILE GLUCOSINOLATE DEGRADATION PRODUCTS IN RAPESEED OIL

Concentration range (mg kg^{-1})	*Mean concentration (mg kg^{-1})*	*n*	*Repeatability (mg kg^{-1})*	*Standard deviation of repeatability (mg kg^{-1})*	*Relative standard deviation of repeatability (%)*
1-Cyano-3-butene					
13–81	40.0	6	0.260	0.092	0.23
3.0–9.0	5.43	20	0.051	0.018	0.33
1.9–2.9	2.40	20	0.036	0.013	0.53
0.32–0.71	0.489	22	0.021	0.007	1.48
0.11–0.23	0.161	16	0.025	0.0089	5.51
0.027–0.082	0.052	12	0.0112	0.0039	7.60
0.010–0.020	0.013	12	0.0075	0.0025	19.00
1-Cyano-4-pentene					
16–41	24.8	8	0.090	0.032	0.13
3.0–5.6	4.01	24	0.051	0.018	0.45
1.3–2.9	1.82	14	0.048	0.017	0.94
0.33–0.97	0.500	32	0.022	0.008	1.59
0.10–0.28	0.195	16	0.012	0.0040	2.16
0.030–0.084	0.052	10	0.0060	0.0020	3.85
0.010–0.021	0.019	10	0.0064	0.0023	11.89
3-Butenyl isothiocyanate					
2.0–12.7	5.07	24	0.031	0.011	0.22
0.32–0.84	0.68	22	0.045	0.016	2.34
0.10–0.28	0.157	22	0.016	0.006	3.60
0.031–0.089	0.0451	24	0.0090	0.0032	7.08
0.010–0.022	0.019	12	0.0080	0.0028	14.89
4-Pentenyl isothiocyanate					
1.3–2.8	1.69	12	0.037	0.013	0.78
0.9–1.2	1.07	10	0.063	0.022	2.06
0.26–0.50	0.33	20	0.047	0.016	4.95
0.044–0.092	0.071	14	0.0046	0.0016	2.31
0.010–0.036	0.022	22	0.0033	0.0012	5.50

detection limits according to Kaiser[4] and limits of determination[5] are given in Table I, and show that the method was sufficiently sensitive for the analysis of crude rapeseed oils and for the evaluation of their refining. However, the procedure is not sufficiently sensitive for the determination of trace amounts in deodorized oils. Improper deodorization can be detected with satisfactory sensitivity.

Repeatabilities of the determination of the most important isothiocyanates and nitriles are given in Table II for several concentration levels. They were calculated from large series of duplicate analyses following the standardized procedure[6].

The main advantages of the above procedure are its simplicity and speed; the duration of an analysis, including the sample preparation, does not exceed 10 min, whereas with FID the samples have to be distilled with water vapour, the distillate extracted with diethyl ether and the extract concentrated before the analysis. Many

other compounds, mainly volatile oxidation products, interfere when FID is used[7] (Fig. 1C); hence NPD is more reliable than FID.

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