STRUCTURE OF THE TRIACYL- AND EPOXYACYLDIACYLGLYCEROLS OF THE SEEDS OF *Galeopsis bifida*

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We have previously reported the isolation from the seeds of *Galeopsis bifida* Boenn. of normal triacylglycerols (n-TAGs) and of epoxyacyldiacylglycerols (ep-TAGs) and have given the structure of the epoxy acids [1]. We now present the results of a stereospecific analysis of these TAGs by Brockerhoff's method [2]. The diacyl glycerols (n-DAGs) were obtained from n-TAGs by pancreatic hydrolysis and were isolated by preparative TLC under conditions described previously [3].

Assuming that the oxirane ring can open in individual steps of the analysis with the formation of hydroxy groups subsequently reacting with the phosphorylating reagent, the ep-TAGs were first converted into the diacetoxy derivatives (diac-TAGs) as described in the literature [1, 4]. The lipolysis of these derivatives did not take place under the usual conditions [3] nor with a change in the certain parameters of the reaction (time of lipolysis, amount of lipase, degree of emulsification), and therefore the diac-DAGS were obtained by added ethylmagnesium bromide in small portions to the diac-TAGs, shaking, and cooling to 0°C for 10 min. The subsequent working up of the products was carried out as described by Christie [4].

To identify the hydrolysis products of the diac-TAGs we used the analogous hydrolysate of the n-TAGs of cottonseed oil, and also the products of the reaction of the acetoxy derivative of ricinoleic acid methyl ester (ME) with a Grignard reagent.

By TLC on Silufol in the petroleum ether–diethyl ether (4:7.5) system of the compounds more polar than the n-TAGS in a hydrolysate of the diac-TAGs we detected three components which we have assigned to the n-monoacylglycerols (n-MAGs) (R_f 0.29), diac-DAGs (R_f 0.23), and diac-MAGs (R_f 0.10). The diac-DAGs were isolated by PTLC on silica gel with 5% of H_3BO_3 in the same system.

The phosphorylation of the n-DAGs and diac-DAGs and the purification and the phospholipolysis of the phosphatidylphenols (PPs) of the n-DAGs were carried out as described previously [3]. The diac-PPs were purified on a column of silica gel L 100/160, from which they were eluted by chloroform–methanol (3:2). The products of the phospholipolysis of the diac-PPs were separated by PTLC on silica gel in the chloroform–methanol–acetone–ammonia (1:2:2:1) system, a lyso compound with R_f 0.08 being isolated.

The MEs of the fatty acids present in the sn-1 and sn-2 positions of the n-TAGs were analyzed by GLC under conditions described previously [3]. The MEs of the fatty acids isolated from the diac-TAGs in the final stages of the analysis in the form of dihydroxy compounds were converted into trimethylsilyloxy derivatives (TMS derivatives) [1], and analyzed by GLC in a column (120 × 0.4 cm) containing 5% of SE-30 on Chromaton N-AW at 220°C at a rate of flow of He of 0.69 kg/cm^2. Under these conditions the di-TMS derivatives of the 18:1 and 18:2 acids have C_{sp} (relative to the 16:0 derivatives) of 5.03 and 6.28, respectively. As a result of the analysis the following distribution of acids in the n-TAGs and p-TAGs was found:

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Acid, mole %

	16:0	18:0	18:1	18:2	18:3
n-TAG	2,9	,0	20,1	51,4	24,6
sn-1	7,3	2,4	25,1	44,8	20,4
sn-2	0,5	—	24,6	55,6	19,3
sn-3	0,9	0,6	10,6	53,8	34,1

Acid, wt. %

	16:0	C_{18}	*epoxy-18:1*	*epoxy-18:2*
ep-TAG	5,0	62,0	11,7	21,3
sn-1	13,3	29,0	9,2	48,5
sn-2	1,6	78,1	14,5	5,8
sn-3	0,1	78,9	11,4	9,6

Consequently, in the n-TAGs almost the whole amount of the saturated acids is present in the sn-1 position, the 18:1 acid is distributed mainly in the sn-1 and sn-2 positions, the 18:2 acid in the sn-2 and sn-3 positions, and the 18:3 acid in the sn-3 position. The nature of the distribution of the 16:0 acid in the ep-TAGs is the same as in the n-TAGs. The epoxy acids, esterifying all three positions, are distributed differently according to their unsaturation: The ep-18:1 acid esterifies mainly the sn-2 and sn-3 positions, and the ep-18:2 acid the sn-1 position.

Thus, we have performed a stereospecific analysis of plant p-TAGs for the first time and have shown that the ep-18:1 and ep-18:2 acids have different natures of their distribution over the three sn-positions of glycerol.

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OIL AND CARBOHYDRATES OF THE SEEDS OF *Cydonia oblonga*

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We have studied the oil and carbohydrates of the seeds of *Cydonia oblonga* Mill. (common quince), family Rosaceae, which are wastes of the preserving industry.

The seeds dried to the air-dry state had an oil content on the absolutely dry matter of 29.3%. According to the literature [1], this magnitude is between 15 and 20%.

The oil and carbohydrates were extracted successively from a single sample of the raw material. The seeds were ground and the oil was extracted by steeping in hexane at room temperature. Then the meal was dried and used for the subsequent extraction of various groups of carbohydrates, mono- and oligosaccharides, water-soluble polysaccharides, pectin substances [2], and hemicelluloses A and B [3]. The polysaccharides were hydrolyzed with 2 N H_2SO_4 at 100°C for 30 h, and the sugars in the hydrolysate were studied by the PC and GLC methods [4], using authentic samples for identification. For GLC, the monosaccharides were converted into the corresponding aldononitrile acetates.

The oil obtained (after the elimination of the hexane) consisted of a mobile light brown liquid with the following indices: $d_4^{20} = 0.9236$ g/cm²; refractive index, $n_D^{20} = 1.4728$; iodine number, 120% I_2; amount of unsaponifiables, 0.94%.

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