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## **Study of rapeseed oil gelation induced by commercial monoglycerides using a chemometric approach**

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## ABSTRACT

Commercial oleogelators rich in monoglycerides (MGs) are complex mixtures of acylglycerides with variable gelling properties, depending on the oil used and their concentration. In this study we developed a chemometric approach to identify the key parameters involved in gelling process. Analytical parameters have been defined, using GC and NMR analysis to identify fatty acids and acylglycerides composing the mixtures. Specific acylglyceride families and compound ratios were calculated to streamline the analytical results. To determine the key analytical parameters, artificial neural networks were used in a QSPR study related to the gelling properties measured by rheology through oscillatory experiments. At low oleogelator concentrations, the MGs especially rich in C16:0 and the ratio of specific isomers both have a positive influence on  $G'$ . For high oleogelator concentrations, C18:0-rich acylglycerides and unsaturated/saturated fatty acid ratios have a positive influence on  $G'$ . Conversely, at low concentrations, C18:0-rich acylglycerides show a lesser effect on  $G'$ .

### 1. Introduction

Fats and oils are largely used as main ingredients in food preparations. Because of their high composition in saturated fatty acids (FAs), the fats are solids at room temperature and this useful property is responsible for the sensory attributes of numerous products (Marangoni et al., 2012). Due to the development of cardiovascular diseases as well as environmental concerns (in the case of palm oil), hard fats are increasingly disliked by consumers and manufacturers (Hooper et al., 2020; Khatun et al., 2017). Besides, some saturated FAs have been implicated in adverse effects to health, such as *trans*-FAs (Booker & Mann, 2008). For all of these reasons, there is nowadays a real demand for solid lipids and consequently there is

25 growing interest in oil structuring alternatives for food industry (Doki et al., 2017; Martins et  
26 al., 2018, 2020; Patel, 2018; Patel et al., 2020; Pehlivanoglu et al., 2018; Puscas et al., 2020).  
27 Oleogelation is a promising technology used in food chemistry to design soft matter structures  
28 with new properties in which the liquid oil is entrapped through the formation of a three-  
29 dimensional network. The oleogelators used to form oleogels can be classified into different  
30 structuring networks: self-assembly fibers (12-hydroxystearic acid, lecithins with  $\beta$ -  
31 sitosterol), crystalline particles (waxes, monoglycerides (MGs)), and polymeric gelators like  
32 cellulose derivatives such as ethyl cellulose, carboxymethyl cellulose and hydroxyl propyl  
33 methyl cellulose (Doan et al., 2018; Han et al., 2013; Meng et al., 2019; Naeli et al., 2020;  
34 Palla et al., 2017; Rogers et al., 2009). Among the food grade oleogelators, MGs are very  
35 interesting for their gelation properties, but also from an economic point of view (Co &  
36 Marangoni, 2012; Yu et al., 2012). These gelators also have the ability to structure both oily  
37 and aqueous phases (Sein et al., 2002). For all these reasons, oil gelation by MGs for food  
38 applications has been the subject of numerous studies (Giacomozzi et al., 2018; Kouzounis et  
39 al., 2017; Palla et al., 2017). Below a critical gelation temperature, MGs can form compact  
40 reverse lamellar phases which will lead to lamellae or platelets. The latter will then assemble  
41 into crystalline clusters which will be able to percolate and form a three-dimensional network  
42 that will entrap the oil (gelation) (Marangoni & Garti, 2011). Gelation is therefore based on a  
43 crystallization phenomenon, and anything that can affect it (ordering or disordering) will  
44 affect the gel and its strength. This phenomenon also depends on the nature of the oil (Ferro et  
45 al., 2019), the MGs concentration (Ojijo et al., 2004), and their intrinsic structure (Cerqueira  
46 et al., 2017). The long chain length and the degree of unsaturation play an important role in  
47 the gelation process (Vereecken et al., 2009).

48 Commercial MGs for industrial use (even relatively pure) are synthesized from natural  
49 products (vegetable oils) and remain complex mixtures composed of different chain lengths

50 and unsaturations that are difficult to purify (Nitbani et al., 2020). In addition, they are  
51 generally mixed with variable amounts of residual diglycerides (DGs) (and their respective  
52 isomers), triglycerides (TGs) and free FAs; all compounds present different chain lengths and  
53 degrees of unsaturation. Consequently, all these ingredients and their structures can mutually  
54 influence the gelation process. The mechanisms involved in oil gelation by DGs oleogelators  
55 involve several steps of crystallization, which are influenced by their isomer structures. In  
56 specific mixtures containing two isomers of 1,2- and 1,3-DGs, significant differences in the  
57 strength of the hydrogen bonds of the hydroxyl groups and the aliphatic chains, related to the  
58 specific three-dimensional arrangements, are observed: V-shaped FA chain arrangement for  
59 1,3-DGs and hairpin-shaped conformation for 1,2-DGs (Lo et al., 2008). MG structures will  
60 also influence crystallization mechanisms based on their saturated and unsaturated FA  
61 composition and their chain lengths (da Silva et al., 2017). Different pure MGs, and  
62 commercial food-grade mixtures of MGs, have also been studied for their gelation properties  
63 with vegetable oils, showing a link between the mixture's composition and rheological  
64 properties (López-Martínez et al., 2014). To date, studies concerning the gelation of oil with  
65 commercial MG products have not been fully described considering the positive or negative  
66 interactions related to the structure and the composition of all the species present in the  
67 mixture: TGs, MGs, 1,2- and 1,3-DGs, and FA composition. The mechanisms involved in  
68 structuring acylglyceride (AG) oleogelators within the oil matrix are complex and not fully  
69 understood. The first step is the solubilization of the oleogelator molecules by the liquid oil  
70 phase at high temperature, followed by the crystallization of the oleogelators while cooling,  
71 reducing the mobility of the oil within a structured network. The properties of this structured  
72 network can be studied using rheological measurements (Patel et al., 2015). The oleogelator  
73 aggregates can act as building blocks to trap the liquid oil into a gel or a gel-like structure,  
74 depending on the nature and concentration of the oleogelators. The structure of the building

75 blocks is stabilized by weak interactions such as H-bonding or dipole. Depending on the  
76 nature of these interactions, different types of aggregates will be formed at the microscopic  
77 scale, resulting in strong or weak structures, and producing viscous liquids or gels at the  
78 macroscopic level that can be studied in the linear viscoelastic region (Fayaz et al., 2020). The  
79 analysis of complex mixtures of AGs is a difficult challenge, and the analytical strategy for  
80 characterizing the composition of mixtures must be defined between targeted and non-  
81 targeted methods. Recently, we have developed a targeted method based on high-resolution  
82 mass spectrometry and liquid chromatography to identify each component of acyl-  
83 polyglycerol, transposable to commercial MGs characterization (Garrigues et al., 2020). Due  
84 to the unknown origin of the commercial MGs, we have chosen in the present study to  
85 evaluate a non-targeted analytical methodology based on proton Nuclear Magnetic Resonance  
86 ( $^1\text{H}$  NMR) and gas chromatography (GC). The composition of the commercial MGs was  
87 determined by quantification of AGs families, determination of the different FAs present in  
88 these mixtures and the calculation of the ratio between these different analytical descriptors.  
89 This analytical methodology was then used to study the gelation of rapeseed oil with different  
90 concentrations of commercial MGs. This oil was specifically chosen due to its health and  
91 nutritional benefits, with its high concentration in both oleic and alpha-linolenic acids  
92 (Vingerling et al., 2010; Xie et al., 2019). The classification of the commercial MGs was  
93 achieved through the use of a quantitative structure/composition properties relationship  
94 (QSPR) by artificial neural networks (ANNs) and multivariable linear regressions (MLRs)  
95 supported by analytical parameters obtained by GC and  $^1\text{H}$  NMR. Several ratios between  
96 specific chemical classes of lipids were introduced, in addition to analytical parameters such  
97 as structure and composition descriptors. All these factors were used to relate the gelation of  
98 rapeseed oil to molecular data, evaluated by rheological measurements ( $G'$ ). For a wider  
99 investigation of the gelation properties, we used thirteen different commercial MGs mixtures.

## 100 2. Materials and methods

### 101 2.1 Chemicals and reagents

102 Rapeseed oil (density at 20 °C = 0.92; viscosity = 80 cP) was used as the liquid oil for all  
103 dispersions with commercial mixtures of mono and diglycerides (MDGs) and was purchased  
104 in a convenience store (METRO®). The commercial MDGs used in this study come from  
105 several providers: MDG 0096, MDG 5616, MDG 0298 and MDG 0051 (Palsgaard), Lamemul  
106 K 2000 K (BASF), Multec Mono 9202 (Puratos) and the medium-chain MDGs (type I & type  
107 II), glycerol dibehenate, glycerol monostearate as well as hemi-synthetic glycerides (HS-  
108 glycerides) (Stearinerie Dubois). Type I medium-chain MDGs are richer in C10:0 FA than  
109 Type II. These distilled MDGs are obtained from edible vegetable oil. All these emulsifiers  
110 are specifically purified and produced for use in food applications. Various reactants were  
111 used for the specific analyses. Sodium methoxide, sodium hydroxide, boron trifluoride,  
112 isooctane and methanol were provided by Sigma Aldrich. The solvent for <sup>1</sup>H NMR analyses,  
113 deuterated chloroform, CDCl<sub>3</sub> (>99.5%), was purchased from Eurisotop.

114

### 115 2.2 Analysis of the commercial AGs mixtures by GC

116 All MDG characterizations were conducted at ITERG (Institut des Corps Gras, Pessac,  
117 France). All analyses were performed in triplicate.

#### 118 2.2.1 Procedure for medium-chain MDGs

119 Transesterification was performed with sodium methoxide (5% w/w). Methyl esters were  
120 analyzed on a GC apparatus (Agilent 6800) equipped with a split/splitless injector, an FID  
121 detector and a CP-Sil 88 polar column (100 m/0.25 mm/0.2 µm). Injector temperature: 250  
122 °C; injection ratio: 1/10; FID temperature: 275 °C. The temperature program was: 60 °C for 5  
123 min; temperature ramp 1: 15 °C/min until 165 °C; temperature ramp 2: 2 °C/min until 225 °C

124 followed by a constant temperature for 20 min as the final step. The results were obtained  
125 after applying a specific response factor to each FA methyl ester. Quantification was carried  
126 out using the C11 methyl ester as the internal standard. All values are expressed with a  
127 minimum and a maximum deviation of 0.5 and 3.5%, respectively.

### 128 2.2.2 Procedure for long-chain MDGs

129 Fat saponification was achieved by a reflux with 0.5M NaOH in methanol and  
130 esterification was performed with 14% boron trifluoride (BF<sub>3</sub>) in methanol. The samples were  
131 then dissolved in isooctane and analyzed on a CP-Sil 88 polar column (100 m/0.25 mm/0.2  
132 μm). Samples were injected according to the following program: injection pressure: 225 KPa;  
133 injector temperature: 250 °C, detector: 275 °C, injection ratio: 1/100. The temperature  
134 program was: oven at 60 °C for 5 min, temperature ramp 1 at 15 °C/min until 165 °C,  
135 temperature ramp 2 at 2 °C/min for 1 min and a constant temperature at 225 °C for 20 min as  
136 a final step. The results were obtained after applying a specific response factor to each FA  
137 methyl ester. Quantification was carried out using the C17 methyl ester as the internal  
138 standard. All values are expressed with a minimum and a maximum deviation of 0.5 and  
139 3.5%, respectively.

### 140 2.3 Analysis for the commercial acylglyceride mixtures by <sup>1</sup>H NMR

141 A known amount of each MDGs was diluted with 700 μL of CDCl<sub>3</sub>, mixed and then  
142 transferred to a 5-mm NMR tube. The 1D <sup>1</sup>H NMR experiment was acquired on a Bruker  
143 Avance 500 spectrometer (Bruker Biospin) equipped with a dual <sup>1</sup>H-<sup>13</sup>C TCI cryoprobe at 25  
144 °C. A conventional NMR pulse sequence with a relaxation delay of 6.54 s, a flip angle of 30°  
145 and an acquisition time of 5.46 s was used. NMR data were processed using the Topspin 4.08  
146 software (Bruker Biospin) with one level of zero-filling and Fourier transformation after  
147 multiplying FIDs by an exponential line-broadening function of 0.3 Hz. Phase adjustment and

148 polynomial baseline correction were done manually on each spectrum. All experiments were  
149 performed in duplicate and the deviation between experiments never exceeded 5%.  
150 Integration was performed on the CH group of the glycerol moiety, at 3.9 ppm (1-MGs), 4.9  
151 ppm (2-MGs), 5.1 ppm (1,2-DGs), 4.1 ppm (1,3-DGs) and 5.3 ppm (TGs). The percentage of  
152 each type of molecule was estimated by dividing the area of its NMR signal by the total area  
153 of all integrations.

154

#### 155 2.4 Preparation of the gels

156 Mixtures of MDGs at different concentrations (from 2.5 to 20 g/100 g) were prepared by  
157 dispersing MDGs (in a liquid, paste or powder form) in rapeseed oil. All the mixtures were  
158 warmed at 80 °C for 1 hour. At this temperature, and after manual mixing, all solutions  
159 appeared isotropic. The samples were stored at 20 °C and some of them became more or less  
160 turbid upon cooling, obtaining numerous textures from liquid to solid. Samples were then  
161 analyzed by rheology after a crystallization equilibrium period (i.e. 1 week).

#### 162 2.5 Characterization of the mixtures by rheological measurements

163 Oscillatory experiments were performed at 20 °C with an ARG2 rheometer (TA  
164 Instruments) on MDG/oil mixtures. All experiments were conducted in a common linear  
165 regime valid for high and low textures, as previously described for the study of hard and soft  
166 oil gels (Fayaz et al., 2020) at a deformation amplitude of 0.1%, and at a frequency of 0.5 Hz.  
167 Parallel-plate geometry was used with a gap of 1 mm and rough surfaces in order to avoid  
168 wall slipping. The MDG/oil mixtures were placed in the cell of the rheometer very carefully;  
169 sample compression during loading was the minimum possible and was always done at the  
170 smallest rate. Excess sample was gently removed from the edge of geometry and the whole  
171 apparatus was covered during the analysis (global time: 2.5 min with a storage modulus

172 acquisition ( $G'$ ; Pa) every 5 s). Temperature within the sample was controlled with a precision  
173 of 0.1 °C via a thermoelectric Peltier module. All rheological measurements were conducted  
174 in triplicate and the deviation between experiments never exceeded 5%.

## 175 2.6 Analytical database

176 An analytical database was constructed for each commercial AG mixtures by integrating  
177 the GC results: FA levels: C6:0; C8:0; C10:0; C12:0; C14:0; C15:0; C16:0; C16:1; C17:0;  
178 C17:1; C18:0; C18:1; C18:2; C18:3; C20:0; C20:1; C22:0; C22:1; C24:0; saturated FAs;  
179 monounsaturated FAs; polyunsaturated FAs and trans FAs. From these raw GC data, specific  
180 analytical parameters were calculated: intermediate FAs (6 to 10 C); long-chain FAs (12 to 22  
181 C) and very long-chain FAs (> 22 C).  $^1\text{H}$  NMR data were introduced for the determination of  
182 the amount of the different AGs and their isomers: TGs; 1,2-DGs; 1,3-DGs; 1-MGs; 2-MGs.  
183 Specific ratios were calculated from the raw GC data: unsaturated/saturated FAs;  
184 monounsaturated/saturated FAs; monounsaturated/polyunsaturated FAs; FAs  
185 polyunsaturated/saturated; long-chain/intermediate FAs; very long/long-chain FAs; long  
186 chain/intermediate FAs; intermediate/long-chain FAs; intermediate/very long-chain FAs;  
187 long-chain/very long-chain FAs. Specific ratios were also calculated from the raw  $^1\text{H}$  NMR  
188 data, and to take into account the low concentrations of certain AGs classes, the inverse ratios  
189 were calculated: MGs/DGs; MGs/TGs; DGs/MGs; DGs/TGs; TGs/MGs; TGs/DGs; 1-MGs/2-  
190 MGs; 2-MGs/1-MGs; 1-MGs/DGs; 1-MGs/TGs; 2-MGs/DGs; 2-MGs/TGs; 1,2-DGs/1,3-  
191 DGs; 1,3-DGs/1,2-DGs; 1,2-DGs/MGs; 1,3-DGs/MGs; 1,2-DGs/TGs; 1,3-DGs/TGs; 1-  
192 MGs/1,2-DGs; 1-MGs/1,3-DGs; 2-MGs/1,2-DGs; 2-MGs/1,3-DGs. If the denominator of one  
193 of these ratios is zero, the ratio was not calculated and a null value was assigned to it.

## 194 2.7 Chemometrics and statistical analysis

195 All data obtained in this study were normalized by dividing each variable by the greatest  
196 value of the column. The QSPR study by ANNs was carried out in MATLAB R2020b  
197 (MathWorks) with the deep learning toolbox V.14.1. An ANN was constructed with 64 input  
198 neurons, connected to each of the 64 analytical parameters and one output neuron connected  
199 to the G' value measured for the 5 concentrations of each of the 13 commercial AGs.  
200 Feedforward backpropagation was used as a learning algorithm, with a sigmoid transfer  
201 function. No hidden layer was used to extract, after 25 learning cycles, the weight attributed  
202 by the ANNs to each of the 64 analytical parameters.

203 Multiple linear regression models were built in MATLAB R2020b, with the statistics  
204 and machine learning toolbox V.12.0, using the key analytical parameters identified by the  
205 ANNs. For each model, the coefficient of determination ( $R^2$ ), the root-mean-square error  
206 (RMS) and the p-value from Fisher's test were calculated from the normalized values.

207 Principal component analysis (PCA) works by using combinations of variables to  
208 describe the variance of a matrix by projecting it on different components. Eigenvectors  
209 represent each variable in a correlation matrix for all components, and the commercial AGs  
210 can be plotted on the corresponding score plot. PCAs were performed in MATLAB R2020b,  
211 with the statistics and machine learning toolbox V.12.0, using the key analytical parameters  
212 identified by the ANNs as variables for each concentration in commercial AGs mixtures to  
213 construct the components. From all the components of the correlation matrices, 3 were  
214 included in the analyses to perform classification of the 13 commercial AGs mixtures and 3D  
215 plots were defined to represent the correlation score for all concentrations used in the gelation  
216 process.

### 217 **3 Results and discussion**

#### 218 **3.1 Analytical database**

219 First of all, the 13 commercial AGs mixtures composed of 11 known oleogelators and  
220 2 negative controls (C8-C10 where no gelation occurs) were analyzed by GC and <sup>1</sup>H NMR to  
221 identify and quantify each lipid classes. With this information, a structural database was built  
222 with 64 analytical parameters (Table S1, supplementary data). To construct Table S1, we  
223 selected the analytical parameters suitable for describing the structure of AGs mixtures,  
224 grouped into 4 families: the lipid class of FAs, the composition of FAs, the amount of TGs  
225 and the different isomers of DGs and MGs and the ratios calculated between these different  
226 structural descriptors. The ratios calculated allow a relative comparison of the commercial  
227 AGs mixtures and any unknown minor impurities are not taken into account for the QSPR  
228 study, which may, in this case, ignore them (Cherkasov et al., 2015).

229

230 The composition of the FAs classes monounsaturated, long, intermediate and the  
231 corresponding AGs varies widely depending on the mixtures investigated. Some analytical  
232 descriptors (Table S1, supplementary data) show high variability in the composition of the  
233 oleogelators, with saturated FAs varying from 7.9 to 99.9 g/100g, mono-unsaturated FAs  
234 ranging from 0.06 to 83.3 g/100g, intermediate FAs (C6-C10) varying from 0.1 to 99.6  
235 g/100g and long-chain FAs (C12-C22) varying from 0.07 to 99.8 g/100g. This composition  
236 is responsible for a variable gelation effect on rapeseed oil when varying the concentration in  
237 the media, as shown in Table 1. A specific codification was applied in this case: 0 means no  
238 gelation; 0.5: liquid-solid equilibrium with flowing and 1: strong gelation with a solid  
239 appearance and no oil clearance after crystallization.

240 Macroscopic analyses of the inverted tube are obtained after 24 hours by visually  
241 observing the structure of the oil formulated with increasing concentrations of the 13  
242 oleogelators.

243 Table 1. Macroscopic observations of the physical state of oily mixtures at room  
 244 temperature after 24 hours, made with a growing amount of commercial AGs mixtures.

Concentrations of AGs mixtures (wt. %)

AGs mixtures	Sample code	Concentrations of AGs mixtures (wt. %)				
		2.5	5	10	15	20
C8-10 MGs intermediate Type II	AG1	0	0	0	0	0
C8-10 MGs intermediate Type I	AG2	0	0	0	0	0
Lamemul	AG3	1	1	1	1	1
MDG 0096	AG4	1	1	1	1	1
Glyceryl dibehenate	AG5	0	0.5	1	1	1
HS-glycerides	AG6	0	0	0.5	0.5	1
Glycerol monostearate	AG7	0	0.5	1	1	1
MDG 5611	AG8	0.5	1	1	1	1
MDG 0091	AG9	0	1	1	1	1
MDG 0298	AG10	0	0	0.5	1	1
MDG 0051	AG11	0	0.5	1	1	1
MDG 5616	AG12	0	0.5	1	1	1
Multec Mono 9202	AG13	1	1	1	1	1

245 *0: liquid state; 1: gel state; 0.5: intermediate state, liquid+gel*

246

247 C8-10 MGs intermediate Type I and Type II were selected for their absence of  
 248 gelation, confirmed by the liquid state observed for all concentration in Table 1. The main  
 249 MGs of C8-10 Type I and Type II are 1-MGs (64.4% and 84.4%, respectively, Table S1,  
 250 supplementary data). No unsaturated FAs are found and chain lengths are exclusively limited

251 to C8:0 and C10:0. The other commercial AGs mixtures behave as gelators, showing variable  
252 gelation properties depending on their composition and concentration. We observed two  
253 categories of products: Lamemul, MDG 0096 and Multec Mono 9202, which show high  
254 gelation properties starting from 2.5 wt.%, and the other eight products which start to gelate  
255 the oil only from 5 or 10 wt.% (Table 1). The composition analysis indicates that Lamemul,  
256 MDG 0096 and Multec Mono 9202 have the highest 1-MGs amounts (97.3%, 97.7% and  
257 96.8%, respectively, Table S1, supplementary data). Nevertheless, MDG 5616, which also has  
258 a very high 1-MGs concentration (96.0%, Table S1, supplementary data), leads to total  
259 gelation only from a 10% concentration in rapeseed oil. Some oleogelators produce soft gels,  
260 which allow a liquid oil phase to appear if the tubes are inverted. This is the case for Glycerol  
261 dibehenate, HS-glycerides, Glycerol monostearate, MDG 5611, MDG 0298, MDG 0051 and  
262 MDG 5616 for concentrations below 20% (Table 1). Soft gels were defined and studied by  
263 Fayaz et al. (Fayaz et al., 2020) with certain types of MGs for which macroscopic  
264 observations showed the presence of a residual liquid oil phase in the structured sunflower oil.  
265 This observation highlights the complexity of the systems and the importance of the mixing  
266 effects, which are still difficult to study.

### 267 3.2 QSPR by ANNs

268 To study the contribution to gelation of all the identified parameters, we used the  
269 analytical database (Table S1, supplementary data) as input descriptors of the AGs mixtures  
270 in a QSPR study. The first step was done by analyzing the weights assigned by ANNs to each  
271 analytical parameter in relation to the storage modulus ( $G'$ ) of the rapeseed oil media  
272 formulated with AGs mixtures and measured by stress-controlled rheology. Table 2 presents  
273 the results of the  $G'$  measurements for the 13 AGs mixtures studied, based on their  
274 concentration in rapeseed oil. Table S2 (supplementary data) gives the key parameters with  
275 weight above 0.6 for all the concentrations of AGs mixtures in rapeseed oil and Fig. S1

276 (Supplementary data) summarizes all the results with positive and negative contributions to  
277 G' according to the structural data measured by analytical parameters. For concentrations  
278 between 5-15 wt.%, The C16:0 FA chain length of the AGs showed high weights for all the  
279 concentrations studied (2.9, 5%; 2.5, 5%; 5.6, 10%; 3.7, 15%; Table S2, supplementary data).  
280 AGs with C18:0 FA showed a negative contribution at low concentrations of AGs mixtures (-  
281 1.5, 2.5%; -1.0, 5%; Table S2, supplementary data), no contribution for 10 and 15 wt.% and a  
282 positive contribution for the highest concentration tested (1.5, 20%; Table S2, supplementary  
283 data). This observation is in agreement with the fact that crystallization and melting  
284 temperature of MGs increase with chain length (Hagemann & Rothfus, 1988). Nevertheless, it  
285 is more difficult to understand the impact of two carbons of difference (between C16 and  
286 C18) on the gel strength as a function of the concentration. This difference could be due to a  
287 more complex crystallization polymorphism, however, as described for MGs with a chain  
288 length of 18 carbon atoms and longer (Hagemann & Rothfus, 1988). In order to ensure a  
289 classification of the gelation properties of these compounds, it is important to correlate these  
290 FAs to the AGs classes (MG, DG, TG) and to their positions. It appears from this study (Fig.  
291 S1 and Table S2, supplementary data) that the 1,3-DGs/1,2-DGs ratios have a positive effect  
292 (from 0.6 to 2.8; Table S2, supplementary data) for concentrations at 2.5%, 5%, 15%, 20%, as  
293 well as the 1-MGs/1,2-DGs ratio with a positive effect (from 1.7 to 2.7; Table S2,  
294 supplementary data) for 2.5, 5, 10 and 15 wt.%. The first observation is in agreement with the  
295 fact that 1,3-DGs present a more symmetrical molecular structure than 1,2-DGs, and therefore  
296 leads to better crystallization and denser packing (Saitou et al., 2012). The positive effect of  
297 the 1-MGs/1,2-DGs ratio reflects the fact that MGs crystallize better and lead to more  
298 efficient gelation than DGs (Tavernier et al., 2019). Monounsaturated FAs showed a negative  
299 effect for 5% and 10% and, in particular, C18:1 (-1.1, 5%; -1.3, 10%; Table S2,  
300 supplementary data), then C18:2, C16:1, and C20:1 for 10 wt.%. The effect of these

301 unsaturated FAs is also noted by the trans FA parameter with a negative effect (-1.6, 20 wt.%;  
 302 Table S2, supplementary data). Whatever the chain length, the negative effect of unsaturation  
 303 on the crystalline packing of lipids is well known. This was clearly demonstrated, but only  
 304 with MGs (Vereecken et al., 2009). Odd FAs are identified as influencing gelling  
 305 mechanisms. Indeed, C17:0 shows a positive effect at 10 and 20 wt.% (1.1 and 1.6  
 306 respectively) and C15:0, a negative effect at 15 wt.% (-1.1) (Table S2, supplementary data). A  
 307 similar effect is described with n-alkanes, where odd chain lengths are less organized than  
 308 even ones. This phenomenon, however, seems less pronounced for FAs with very long chains  
 309 (Yang et al., 2016). Once again, the observed effect seems to indicate a tipping point for a  
 310 C16 length in our mixtures, with a positive effect for C17 (> C16) and a negative one for C15  
 311 (<C16).

312

313 Table 2. Rheological measurements with  $G'$  (Pa)  $\pm$  Standard deviation of oil mixtures with  
 314 increasing concentrations (2.5-20 wt.%) of the 13 AGs mixtures.

AGs mixtures	AGs mixtures concentrations (wt. %)				
	2.5	5	10	15	20
C8-10 MGs intermediate Type II	0	0	0	0	0
C8-10 MGs intermediate Type I	0	0	0	0	0
Lamemul	2545 $\pm$ 48	19182 $\pm$ 892	451392 $\pm$ 18310	2093831 $\pm$ 86677	3314210 $\pm$ 59761
MDG 0096	133 $\pm$ 4	3624 $\pm$ 159	7443 $\pm$ 284	99251 $\pm$ 2913	291705 $\pm$ 8801
Glycerol dibehenate	143 $\pm$ 4	550 $\pm$ 15	1801 $\pm$ 58	304307 $\pm$ 5975	935502 $\pm$ 35365
HS-glycerides	0	0	0	94 $\pm$ 2	3804 $\pm$ 124
Glycerol monostearate	857 $\pm$ 42	2443 $\pm$ 38	403178 $\pm$ 16372	1566856 $\pm$ 50302	6455613 $\pm$ 108601
MDG 5611	1173 $\pm$ 39	3679 $\pm$ 85	155231 $\pm$ 7175	503483 $\pm$ 16071	894604 $\pm$ 36843
MDG 0091	341 $\pm$ 14	16610 $\pm$ 624	106885 $\pm$ 4218	183001 $\pm$ 1406	201361 $\pm$ 9522

MDG 0298	0	0	0	11393 ± 394	6505423 ± 3488
MDG 0051	28 ± 1	1261 ± 19	4410 ± 104	244577 ± 6585	7742036 ± 156466
MDG 5616	35 ± 2	340 ± 17	739 ± 32	35101 ± 1205	468323 ± 19673
Multec Mono 9202	10663 ± 396	24860 ± 335	268909 ± 8453	2570651 ± 69069	6505423 ± 236792

315

316 All FAs with chain lengths less than C16:0 display significant weights with a negative  
317 influence on  $G'$ . This is valid for C8:0, C10:0, C12:0 and C14:0, and intermediate FAs,  
318 whatever the concentrations studied. This observation confirms the tipping point previously  
319 determined at a C16 chain length.

### 320 3.3 Multiple linear regression models

321 To quantify the combined effects of the different structural parameters, we modeled  
322 the gelation of each AG mixture by crossing the key analytical parameters (Table S2 and Fig.  
323 S1) identified by ANNs, in MLRs, using the smallest number of non-auto-correlated key  
324 parameters. The linear equation determined by the MLR has the form as the form shown in  
325 Eq. (1).

326 Eq. (1).  $G'_{x\%} = a_0 + \sum_{i=1}^4 a_i \times D_i$

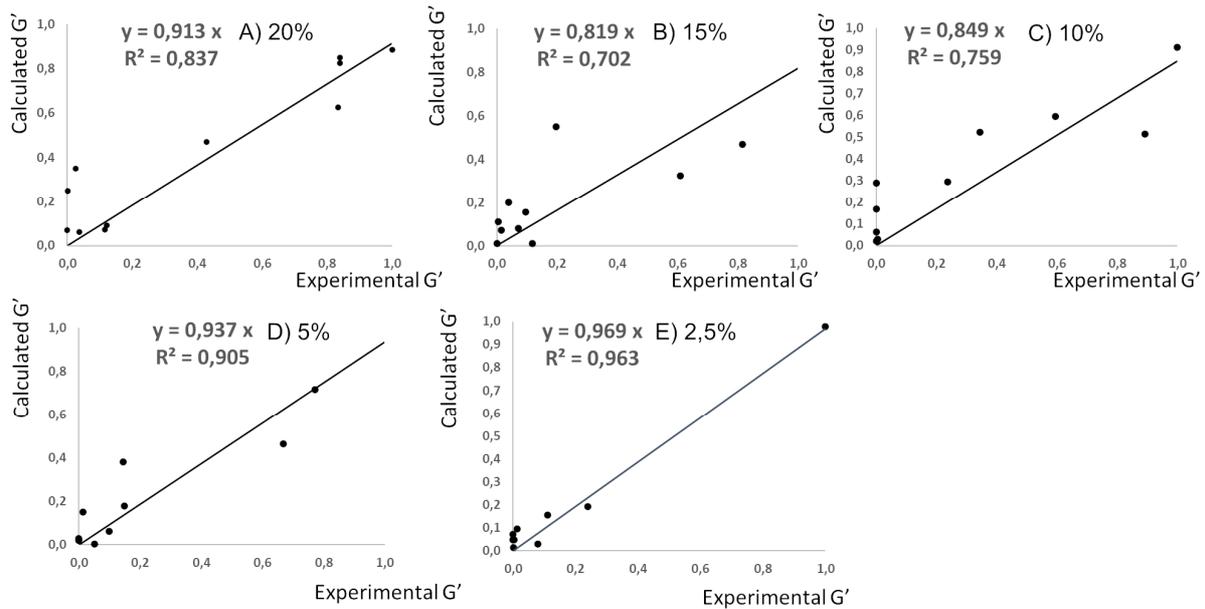
327 where  $G'_{x\%}$  is the elastic modulus measured for the oil mixture at  $x\%$  of gelator (Table 2),  $a_i$   
328 are the parameters determined by least squares and  $D_i$  are the independent analytical  
329 descriptors chosen from Table S1. Table S3 gives the values of the regression parameters, as  
330 well as the model descriptors, for the five mass concentrations investigated in this study.  
331 From 2.5 to 15 wt.%, MLRs show that structural parameters are strictly related to C16:0,  
332 regardless of the AG class.

333 The C16:0 FAs have very high parameter weights for all concentrations, except for 20 wt.%  
334 (0.550, 15 wt.%; 0.921, 10 wt.%; 0.157, 5 wt.% and 0.207, 2.5 wt.%; Table S3) and a positive

335 influence in linear regressions. C16:0-rich oleogelators (Lamemul, MDG5611, Multec Mono  
336 9202) show a strong influence on the structuration of rapeseed oil at the lowest concentration  
337 (2.5%), with measured  $G'$  values greater than 1000 Pa (Table 2). For the highest  
338 concentration of AGs mixtures, the models do not provide a satisfactory regression with  
339 C16:0 and in this case, the C18:0 FAs show a differentiation among the AGs mixtures in  
340 linear regressions with a high weight (0.739) (Table S3). MDG0051, which has the highest  
341 rate of C18:0 (89.8%, Table S1), has the greatest influence on  $G'$  with the highest value  
342 ( $>7.10^6$  Pa, Table 2) obtained for the highest concentration (20%). To complete these models,  
343 it is necessary to combine information on the AG classes. Thus, the 1,3-DGs/1,2-DGs ratio  
344 has a very important positive influence for concentrations of AGs mixtures of 2.5, 15 and 20  
345 wt.% (1.080, 0.742 and 0.663, respectively) (Table S3). For other concentrations, the  
346 MGs/DGs ratio (0.548, 10 wt.%) shows an effect (Table S3) as does 1-MGs/1,2-DGs ratio  
347 (0.935, 5 wt.%) (Table S3).

348 MLRs show the negative influence of unsaturated FAs C18:2 (-0.514, 10 wt.%; Table S3) and  
349 C18:1 (-0.435, 5 wt.%; Table S3). MDG5611, which has a higher rate of C16:0 (59.9 g/100g)  
350 than Lamemul (40.9 g/100g) (Table S1), but a high rate of C18:1 (20.0 g/100g) and lower  $G'$   
351 values for all concentrations (1173 Pa, 2.5%; 3679 Pa, 5%; 155231 Pa, 10%; 503483 Pa,  
352 15%; and 894604 Pa, 20%; Table 2). A difference can be highlighted between mono- and  
353 poly-unsaturated and the ratios of these classes. A positive effect is determined for  
354 unsaturated/saturated FA ratios (0.651, 20 wt.%) (Table S3), while a negative effect is  
355 attributed to monounsaturated/polyunsaturated FA ratios (-0.668, 20 wt.%) (Table S3). We  
356 observed that for high concentrations, unsaturated compounds do not affect gelation, because  
357 the crystalline organization is strong enough and not disturbed by the presence of these  
358 unsaturated chains. In addition, it has been observed that polyunsaturated chains disturb the  
359 organization of the AGs more than the monounsaturated ones (Vereecken et al., 2009). The

360 negative influence of C18:0 FAs is confirmed for low acylglyceride mixture concentrations,  
361 with low weights (-0.101 and -0.019 for 2.5 and 5 wt.%, respectively) (Table S3). The  
362 negative contribution of short-chain FAs is confirmed for intermediate concentrations (C15:0,  
363 -0.311 at 10 wt.%; C12:0 -0.209 at 15 wt.%) (Table S3). The theoretical G' values were  
364 calculated from all MLRs (Eq. (1) and Table S3 for the parameters and descriptors) and  
365 compared to normalized experimental values (Fig. 1). For all models, R<sup>2</sup> is greater than 0.7  
366 for n=13, confirming regressions. The small number of AGs mixtures samples prohibits the  
367 study of interactions between descriptors or external validation, but classification of AGs  
368 mixtures remains possible on the basis of the weights studied by ANNs and confirmed by  
369 MLRs, as shown in Fig. 1. All statistical results are presented in Table S4. For the fitting  
370 validation, all MLRs give R-squared models in the 0.733-0.963 range for n=13 samples and  
371 p=4 or 5 independent analytical parameters. The p-value is below the 5% confidence interval  
372 for all MLRs, in the  $2.9 \cdot 10^{-2}$ -  $8.6 \cdot 10^{-6}$  range. For cross-validation, R-squared for the calculated  
373 G' vs experimental regressions are in the 0.702-0.963 range and the RMS errors are in the  
374 0.003-  
375 0.029 range. All these data provide validation of all the linear regression parameters according  
376 to the statistical criteria for our experimental space. It should be noted that the low number of  
377 commercial AGs makes it impossible to evaluate external cross-validation using different test  
378 and regression datasets. These models can therefore only be used for the analysis of the  
379 interactions of the variables corresponding to the analytical parameters (Gramatica, 2013;  
380 Konovalov et al., 2008).



381

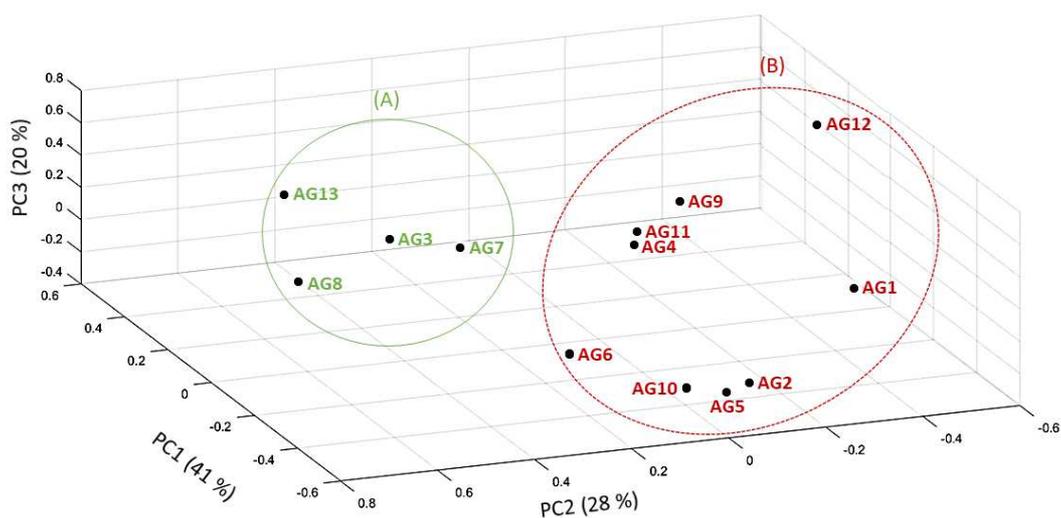
382 Fig. 1. Calculated vs experimental  $G'$  for the 13 AGs mixtures by varying mass  
 383 concentrations from 20 to 2.5 wt.% in rapeseed oil (from A to E, respectively).

384

### 385 3.4 Principal component analysis

386 The principal component analysis (PCA) of rapeseed oil samples gelled with low  
 387 concentrations of each AGs mixture (2.5 wt.%; Fig. 2) shows a group of 4 oleogelators  
 388 (Lamemul: AG3; glycerol monostearate: AG7; MDG 5611: AG8 and Multec Mono 9202:  
 389 AG13) in the same space, defined by the 3 components PC1, PC2 and PC3 representing 90%  
 390 of the observed variance, using C16:0, the ratio 1,3-DGs/1,2-DGs and the ratio 1,2-DGs/TGs  
 391 as the main descriptors favorable to interactions structuring the oil matrix. The positive effect  
 392 of the 1,2-DGs/TGs ratio reflects the better gelling properties of 1,2-DGs compared to  
 393 triglycerides, even if its crystalline organization is less dense than that of 1,3-DGs (Tavernier  
 394 et al., 2019). This group shows that a mixture of AGs containing more than 32 wt.% of C16:0,  
 395 a 1,3-DGs/1,2-DGs ratio greater than 32.510, and a 1,2-DGs/TGs ratio greater than 2.510  
 396 explain the gelling properties at low concentrations. Longer chain FAs (i.e., C18:0) do not

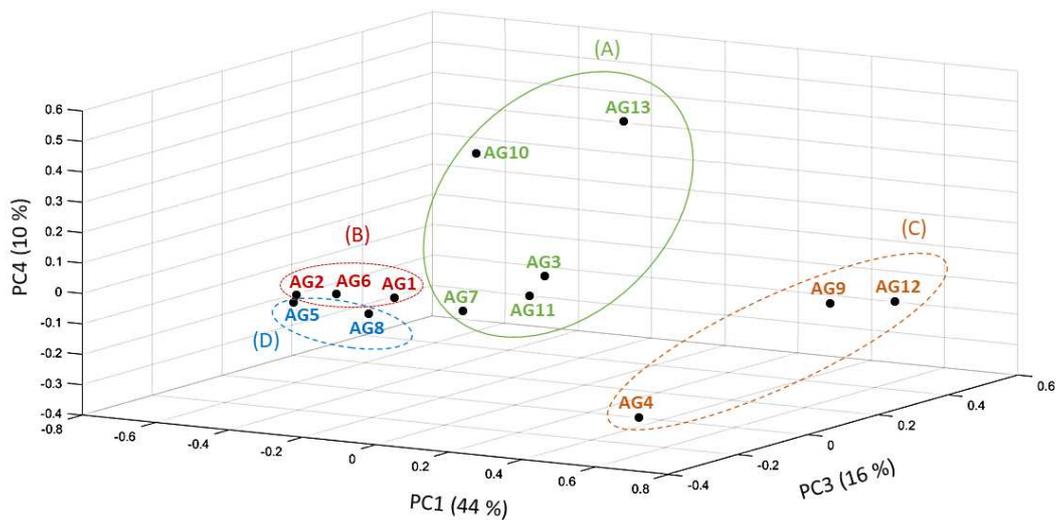
397 explain classification, as the negative contribution of this descriptor indicated in Table S3 (a4,  
 398 2.5%). Thus, MDG 0091 (AG9), MDG 0096 (AG4) and MDG 0051 (AG11), with the highest  
 399 concentrations in C18:0 FAs (ranging from 78.5% to 90.61%) and lower values for the C16:0  
 400 parameters and the 1,3-DGs/1,2-DGs ratio, are classified in the group of weak oleogelators  
 401 (Fig. 2, group B). If the MGs correspond to the major species for most of the AGs studied  
 402 (Table S1, c), Supplementary data), it is clear that DGs can contribute to the classification.  
 403 The 1,3-DGs/1,2-DGs ratio shows that the balance between these two isomers is an important  
 404 factor to be considered for effective oleogelating properties at low concentrations.



405  
 406 Fig. 2. PCA based on the key analytical parameters for 2.5 wt.% of AGs in rapeseed oil  
 407 clustered in high measured  $G'$  values  $> 8 \cdot 10^2$  Pa (A) and low  $G' < 8 \cdot 10^2$  Pa (B).

408 The PCA analysis for the highest concentration of alkyl glycerides (20 wt.%) (Fig. 3.)  
 409 shows a group of 5 oleogelators (Lamemul: AG3; Glycerol monostearate: AG7; MDG 0298:  
 410 AG10; MDG 0051: AG11 and Multec Mono 9202: AG13) in the same space, defined by the 3  
 411 components PC1, PC3 and PC4 representing 70% of the variance observed. These 3 PCs are  
 412 the product of the key parameters identified with MLRs. Among these parameters, C18:0, the

413 unsaturated/saturated FA ratio and the 1,3-DGs/1,2-DGs ratio show a positive weight in the  
414 interactions favorable to G' and obtaining strong oleogels (Table S3). But the negative  
415 contribution of the monounsaturated/polyunsaturated FA ratio and the 2-MGs/TGs ratio must  
416 be taken into consideration to understand the interactions that explain the gelation properties.  
417 In fact, MDG 0051 (AG11, Fig. 3), which gives the highest value of G' for a 20 wt.%  
418 concentration in rapeseed oil ( $7.74 \cdot 10^6$  Pa), shows a very high rate of C18:0 (89.9%) as well  
419 as a high 1,3-DGs/1,2-DGs ratio (3.38), but MDG 0091 (AG9, Fig. 3) with the highest rate of  
420 C18:0 (90.6%) and a high 1,3-DGs/1,2-DGs ratio (2.94) is classified in Group C with an  
421 intermediate G' value ( $2.01 \cdot 10^5$  Pa). The negative contribution of the 2-MGs/TGs ratio for  
422 MDG 0091 (67.0) is much higher than that of MDG 0051 (0.87). It is important to note that  
423 the contribution of C16:0 no longer explains the properties of each AG for a 20 wt.%  
424 concentration. It appears from this classification that C18:0 is not solely responsible for the  
425 good properties of the oleogelators. We also observed that the high weight given to the  
426 unsaturated/saturated FA ratio explains the behavior of MDG 0298 (AG10, Fig. 3). The latter  
427 shows a very low level of C18:0 (2.7%), but the highest unsaturated/saturated FA ratio (11),  
428 related to a very high unsaturated C18:1 FA level (83.0%). Moreover, this oleogelator shows  
429 a very low 2-MGs/TGs ratio (3.81), which gives less of a negative contribution to  
430 interactions. Therefore, it appears that AGs containing C18:1 long-chain FAs, mainly in the  
431 form of MGs, may be considered as efficient oleogelators valuable at high concentrations, but  
432 gelling mechanisms with these same species in the mixture at low concentration (2.5 wt.%)  
433 are not possible (Fig. 2 (B), AG10). This identified high concentration complexity is reflected  
434 in the appearance of the other two G' intermediate spaces (C and D, Fig. 3). Space C contains  
435 3 oleogelators MDG 0096: AG4; MDG0091: AG9 and MDG 5616: AG12, which have high  
436 levels of C18:0, but the three of them have the highest monounsaturated/polyunsaturated FAs  
437 or 2-MGs/TGs ratios of all the AGs studied.

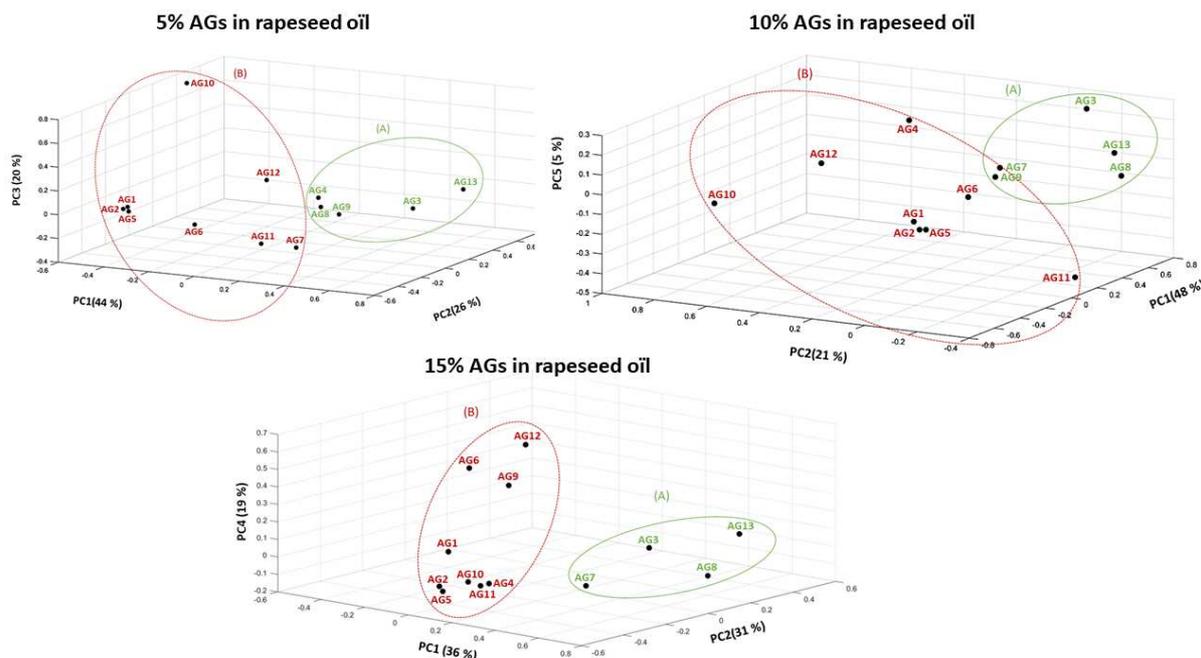


439

440 Fig. 3. PCA based on the key analytical parameters for 20 wt.% of AGs in rapeseed oil  
 441 clustered in high measured  $G'$  values  $> 3.10^6$  Pa (A), low  $G' < 4.10^3$  Pa (B), and intermediate  
 442  $G'$  from  $2.10^5$  to  $5.10^5$  Pa (C) and from  $8.5.10^5$  to  $9.5.10^5$  Pa (D).

443 The experimental space D, very close to the AGs showing no gelling properties at 20  
 444 wt.%, contains glyceryl dibehenate: AG5 and MDG 5611: AG8. Unlike Group C, these AGs  
 445 have very low rates of C18:0 and 1,3-DGs/1,2-DGs ratios. Classification closer to group (B)  
 446 than group (C) is therefore justified.

447 The PCA study of the other 3 concentrations: 5, 10 and 15 wt.% (Fig. 4) shows continuity  
 448 with the study of the 2.5 wt.% concentration. The classification is obtained in two groups  
 449 according to the gelling properties and the  $G'$  values measured (Fig. 4). These 3  
 450 concentrations are classified according to the components PC1, PC2, PC3 representing 90%  
 451 of the variance for 5 wt.%; PC1, PC2 and PC5 representing 74% of the variance for 10 wt.%  
 452 and PC1, PC2 and PC4 representing 86% of the variance for 15 wt.%.



453  
 454 Fig. 4. PCA based on the key analytical parameters for 5 wt.% of AGs in rapeseed oil  
 455 clustered in high measured  $G'$  values  $> 3.6 \cdot 10^3$  Pa (A), low  $G' < 2.4 \cdot 10^3$  Pa (B), 10 wt.%  
 456 clustered in high measured  $G'$  values  $> 1.5 \cdot 10^5$  Pa (A), low  $G' < 7.4 \cdot 10^3$  Pa (B), and 15 wt.%  
 457 clustered in high measured  $G'$  values  $> 5.1 \cdot 10^5$  Pa (A), low  $G' < 2.4 \cdot 10^5$  Pa (B).

458 For each of the MLRs and principal components, C16:0 appears to have a strong positive  
 459 influence on the interactions contributing to  $G'$ , associated with the 1,3-DGs/1,2-DGs ratio for  
 460 5 and 15 wt.% and the MGs/DGs ratio for 10 wt.%. For these intermediate concentrations, the  
 461 influence of C18:1 and C18:2 FAs appears negatively in interactions contributing to  $G'$ .

462

#### 463 4 Conclusion

464 This study shows that the classification of commercial MGs mixtures is possible using  
 465 analytical descriptors based on  $^1\text{H}$  NMR and GC. The use of ANNs made it possible to  
 466 identify the key analytical parameters that influence gelling properties depending mainly  
 467 on the nature of the oleogelator involved and their respective concentrations (from 2.5 to

468 20 wt.%). The oleogelators studied are mainly composed of MGs, among them 1-MGs.  
469 The analytical descriptors used in this study are adapted to this class of lipids and allow  
470 classification without studying the possible synergies induced by the variations in the  
471 minor species, such as the different positions of FAs on DGs or TGs. MLR models have  
472 confirmed the weight and influence of the selected parameters on the gelation and  
473 hardness of the final dispersion. The QSPR study showed that MGs-rich AGs with C16:0  
474 FAs, high 1,3-DGs/1,2-DGs ratios and low intermediate AGs (<C15 FAs) present good  
475 gelling properties at low concentrations up to 15 wt.% in rapeseed oil. The MGs or DGs  
476 containing C18:0 present in these mixtures were not able to contribute positively to  
477 gelation (G') at low concentrations, but were very effective at high concentrations,  
478 especially at 20 wt.%. It appears that these same species contribute negatively to G' at low  
479 concentrations. This study also showed that MGs containing C18:1 strongly contribute to  
480 efficient gelation of the oil at high concentrations, but not at the lowest concentrations,  
481 where they contribute negatively to G'.

482 We have demonstrated that by combining 4 or 5 analytical parameters it is possible to  
483 classify different commercial MGs mixtures according to their gelling properties in  
484 vegetable oil and according to their concentration. This classification showed that 3  
485 products were grouped and can be considered as strong oleogelators for all the  
486 concentrations tested: Lamemul: AG3; glycerol monostearate: AG7 and Multec Mono  
487 9202: AG13.

488 This study demonstrates that the combination of a neural network study associated with  
489 multiple linear regression models and a principal component analysis constitutes a  
490 powerful tool for the study of complex mixtures. Such an approach could be applied to a  
491 large number of fields (food, cosmetics or pharmaceuticals) for industrial applications but  
492 also for a more fundamental comprehension of multiple interactions in complex mixtures.

493

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