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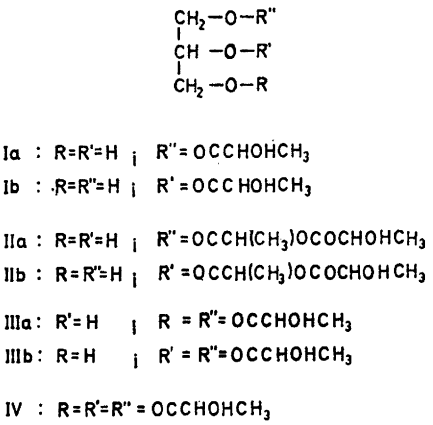


# Mass Spectrometry of Glycero-lacto Esters

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In connection with an investigation of glyceryl-lactyl esters of fatty acids, a type of commercial emulsifying agents, the isomeric glyceryl monolactates (I a, I b), glyceryl-monolactyl lactates (II a, II b), glyceryl dilactates (III a, III b), and glyceryl trilactate (IV) have been prepared in order to study their mass spectroscopic fragmentation.

Prior to mass spectrometry the compounds (I)—(IV) were converted into their volatile *O*-trimethylsilyl (TMS) derivatives, essentially as described by Wood *et al.*,[1] yet without isolation of the individual derivatives. These were merely separated by vapour phase chromatography and introduced directly into a combined mass spectrometer (see Experimental). Fig. 1 portrays the separation of (I a) and (I b), representative of the degree of separation achieved for all TMS-derivatives of (I)—(IV). Table 1 presents the retention times of the derivatives.

The mass numbers (*m/e*) of the most characteristic ions observed as a result of electron impact are presented in Table 2, together with a tentative assignment to the respective ions.

*Table 1.* Retention times of TMS-derivatives of glyceryl lactates.

| Starting material | Physical constants of the starting material | Compound formed | R.t. of the TMS derivative, min |
|---|---|---|---|
| 2,3-Isopropylidene glycerol [3] | b.p. 83.0—83.5°/12 mm | 1-Glyceryl lactate (I a) [3] | 10.7 |
| 1,3-Benzylidene glycerol [5] | m.p. 66.0° | 2-Glyceryl lactate (I b) | 10.3 |
| 1-Lactoyl-2,3-isopropylidene glycerol [3] | b.p. 68.5—70°/0.05 mm | 1-Glyceryl lactyllactate (II a) | 15.3 |
| — | — | 2-Glyceryl lactyllactate (II b) | 15.7 |
| 2-*O*-Benzyl glycerol [6] | m.p. 38—39° | 1,3-Glyceryl dilactate (III a) | 15.6 |
| 1-*O*-Benzyl glycerol [7] | b.p. 152°/1.5 mm | 1,2-Glyceryl dilactate (III b) | 15.3 |
| Glycerol [3] | synthetic (98 % purity) | 1,2,3-Glyceryl trilactate IV [3] | 19.4 |

*Table 2.* Mass spectra of TMS-derivatives of glyceryl lactates.

| *m/e* | Tentative ion assignment | 2-Glyceryl lactate (I b) | 1-Glyceryl lactate (I a) | 2-Glyceryl lactyl-lactate (II b) | 1-Glyceryl lactyl-lactate (II a) | 1,2-Glyceryl dilactate (III b) | 1,3-Glyceryl dilactate (III a) | 1,2,3-Glyceryl trilactate (IV) |
|---|---|---|---|---|---|---|---|---|
| 45 | $H_2Si{\cdot}CH_3$ | 8 [a] | 10 | 2 | 15 | 12 | 14 | 0 |
| 59 | $HSi(CH_3)_2$ | 8 | 10 | 8 | 11 | 12 | 12 | 0 |
| 73 | $Si(CH_3)_3$ | 88 | 83 | 100 | 27 | 90 | 88 | 7 |
| 103 | $CH_2OTMS$ | 40 | 33 | 27 | 29 | 7 | 3 | 0 |
| 117 | $CH_3CH(OTMS)$ | 100 | 100 | 83 | 100 | 100 | 100 | 100 |
| 129 | — | 26 | 16 | 28 | 20 | 62 | 37 | 9 |
| 147 | — | 26 | 36 | 25 | 38 | 22 | 18 | 6 |
| 205 | $CH(OTMS)CH_2OTMS$ | 1.4 | 10 | 2 | 7 | 1 | 2 | 0 |
| 218 | $CH_2CH(OTMS)CH_2OTMS-H$ | 14 | 4 | 9 | 8 | 0 | 0 | 0 |
| 219 | $CH_2CH(OTMS)CH_2OTMS$ | 13 | 11 | 7 | 11 | 5 | 2 | 3 |
| 247 | — | — | — | — | — | 2 | 11 | — |
| M−175 | $M-CH_2OCOCH(OTMS)CH_3$ | 1.4 | 10 | 0.3 | 5 | 2 | 9 | 0.2 |
| M−161 | $M-OCOCH(OTMS)CH_3$ | 13 | 11 | 1 | 0.8 | 18 | 18 | 25 |
| M−145 | $M-COCH(OTMS)CH_3$ | 1 | 0 | 0 | 0.1 | 4 | 1 | 0 |
| M−103 | $M-CH_2OTMS$ | 0.3 | 28 | 0.3 | 16 | 0 | 0 | 0 |
| M−15 | $M-CH_3$ | 0.5 | 3 | 0.8 | 5 | 2 | 1 | 0.5 |

[a] The figures in these columns represent the relative abundance of the ions, arbitrarily assigning the base peak as 100 %.

In no case were molecular ions observed, but low intensity-peaks at M−15, caused by the loss of a methyl group, were consistently present (Table 1). The base peaks occurred at *m/e* 117 in all compounds, save for (II b), and represents the ion $[CH_3CH(OTMS)]^+$, arising from fission of the C−C bonds next to the CO-groups. Another prominent peak at *m/e* 103, virtually absent only in (III a) and (IV), is attributable to the ion $[CH_2O(TMS)]^+$ and hence of diagnostic interest. Alternative charge distribution from the same fission is responsible for the M−103 ions, much more abundant in (I a) and (II a) than in (I b) and (II b) in accord with similar observations by Johnson and Holman [2] in the mass spectra of TMS-derivatives of monoglycerides of fatty acids.

Simple rupture of the acyloxy-carbon bonds in all esters produces ions at *m/e* 219, yet without conspicuous difference

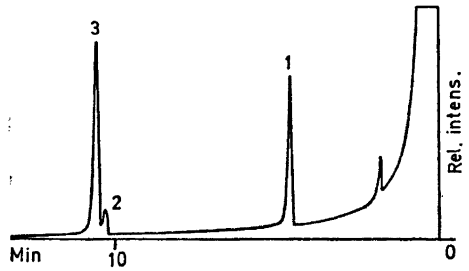
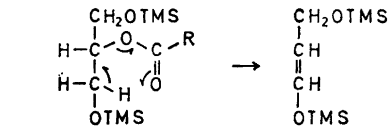
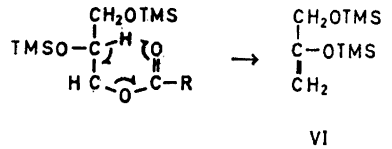



*Fig. 1.* Gas chromatogram of the TMS-derivative of an isomeric mixture of glyceryl monolactates. (1): TMS-glycerol; (2): TMS-2-glyceryl lactate; (3): TMS-1-glyceryl lactate.




V




VI

between the primary and secondary types. Expulsion of a hydrogen atom, or, alternatively, McLafferty rearrangement to (V) and (VI), account for the ions *m/e* 218, with, as expected, somewhat higher abundance of (V) for the monoesters. Fission of the $C_1-C_2$ bond in the glycerol moiety produces an ion, *m/e* 205, which is much more abundant in the primary series and presumably represents the fragment $[CHO(TMS)CH_2O(TMS)]^+$. The above regularities hold for the lactyllactates, (II a) and (II b), whereas the fragmentation patterns for the isomeric dilactates, (III a) and (III b), are virtually identical, save for the presence of a strong peak at *m/e* 247 in (III a). Typical fragments in the isomeric dilactates, (III a) and (III b), as well as in the trilactate, M−161, arise from loss of a TMS-lactyloxy radical from the molecular ion.

By critical evaluation of the above results, mass spectrometry proves to be a powerful analytical tool in identifying the substitution patterns in glyceryl esters of the type here discussed.

*Experimental. Preparation of TMS-derivatives.* The glyceryl ester (10 mg) is dissolved in dimethyl formamide (50 µl), and hexamethyl disilazane (0.15 ml) and glacial acetic acid (10 µl) are added to the solution. After shaking for 30 sec and standing for 2 min at room temperature, the reaction is complete.

*Gas chromatography.* Gas chromatography was performed on a silicon rubber, dual column (2 m × 1/8″ stainless steel, 3 % SE 52 on Gaschrom Z, 80/100 mesh). Conditions: 30 ml He/min; injection block: 300°; column: 100−300°, 6.7°/min; sample: 1.0 µl; detector: FID, 320°; apparatus: Perkin Elmer, Model 880.

*Mass spectrometry.* The exit from the gas chromatograph was attached to a Hitachi-Perkin Elmer, Model RMU-6D mass spectrometer by a 1.5 m × 0.1 mm heated stainless steel tube, and a Biemann-type helium separator. Conditions were: ion source temperature: 250°; ionization potential: 70 eV; scanning speed: 5.8 sec; mass range 12−600.

*Preparation of esters.* None of the esters were prepared in analytically pure state due to thermal instability and ease of isomerization. Except for (II b), they were synthesized in such a way that the desired isomer was formed as the main product besides various amounts of impurities and small amounts of isomers formed during the synthesis. Generally the intermediates were not isolated.

The general procedure of Feldmann and Fischer,[3] as outlined in their synthesis of 1-glyceryl monolactate and 1,2,3-glyceryl trilactate, was used, involving acylation of the appropriate alcohols with *O*-benzyl-lactoyl chloride followed by removal of the protecting benzyl groups by hydrogen and palladium-black, and the protecting isopropylidene groups by a weak acid. In the preparation of (I a) and (II a), however, trimethyl borate/boric acid [4] was used instead of acetic acid.

(II b) was not synthesized since it was formed by isomerization during the last step of the synthesis of (II a), appearing in the gas chromatogram as a smaller peak before a higher one, *cf.* Fig. 1 and Wood *et al.*[1]

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