



Forgotten fatty acids—Surface properties supply conclusive evidence for including carotenoid acids

Asma Zaidi¹, Inger Lise Alsvik², Christer L. Øpstad³, Daniel Martin⁴, Eduard Rebman⁵, Georg Voss⁶, Hans-Richard Sliwka^{*}, Vassilia Partali

Department of Chemistry, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

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ABSTRACT

The term “fatty acids” is conceptually well defined with regard to fats, whose extent of saturation or unsaturation is precisely indicated in the content description of foodstuff. In contrast, the term “fatty acid” gives no hint of being associated with “soap” (Na and K salts of fatty acids). Fatty acids in edible fats or in cleaning soaps have one thing in common: they are colorless. The prevalence of colorless fats and unadulterated white soaps has ensured that fatty acids are not associated with color. However, colored conjugated polyunsaturated fatty acids do exist, occurring abundantly in nature or manufactured at large scale. We endeavor to extricate conjugated polyenoic acids from oblivion by

- presenting new data on surface tension and critical micelle concentration of Na-, K- and Cs-carotenates,
- comparing these data with Na-, K- and Cs-carboxylates,
- revisiting previously synthesized glycol-, glycerol- and phospholipids with carotenoid acids.

Based on the presented results (alkalicarotenates have similar surface properties to alkalicarboxylates, carotenoid acids react like carboxylic acids to lipids), we argue for inclusion of conjugated carotenoid acids in fatty acid inventories and organic chemistry textbooks. Carotenoid acids and –salts have outstanding qualities by combining visibility and traceability with biological activity.

1. Introduction

1.1. Background

Literally speaking, fatty acids define the most prominent constituents of fats. By tradition, alkali salts of fatty acids are the characteristic ingredients of soaps. The term “saturated fatty acids” (truncated C_n:N, n = number of carbon atoms, N = number of double bonds) denotes the trivial name of a vaguely specified fraction of carboxylic acids covering the range from C1:0 (formic acid) to C192:0 (dononacontahectanoic acid), Note S1. (Brooke et al., 1996) Unsaturated fatty acids include essentially monoene to hexaene compounds, in which –C=C–bonds are separated by –CH₂– groups. Series

of conjugated polyunsaturated acids are restricted, since double bond accumulation provokes increasing instability e.g. acrylic acid series C3:1–C7:3, crotonic acid series C4:1–C16:7. (Smakula, 1934; Pini et al., 2008) Deterioration starts noticeably with N = 3 (octatrienoic acid C8:3, linolenic acid 18:3) (Kuhn and Hoffer, 1930; Kawahara et al., 2012). and acids with N ≥ 4 (e.g. parinaric acid C18:4, ajoenic acid C12:5, hexacosahexaenoic acid C26:6) can hardly be isolated (Sklar et al., 1981; Cason et al., 1971; Patalag and Werz, 2012). With these facts in mind the recently reported isolation of laetiporic acids with N = 12 appeared as an inconceivable surprise (Davoli et al., 2005). Labile conjugated polyenoic acids were synthesized 80 year ago (Kuhn, 1938); conjugated polyunsaturated fatty acids stabilized with in-chain methyl-branches and cyclohexene end-rings were apparently

* Corresponding author.

E-mail address: richard.sliwka@ntnu.no (H.-R. Sliwka).

¹ Present address: COMSATS University, Department of Chemistry, Abbottabad Campus, Pakistan.

² Present address: SAR AS, Oljeveien 5, 4098 Tananger, Norway.

³ Present address: Powder Coatings, Jotun AS, 3202 Sandefjord, Norway.

⁴ Present address: Technische Entwicklung, Pass GmbH, Berliner Str. 11, 58332 Schwelm, Germany.

⁵ Present address: LPGC, CNRS/CPE Lyon/UCBL-Université de Lyon, 43 Boulevard du 11, Novembre 1918, 69616 Villeurbanne, France.

⁶ Present address: NTNU, Department of Geoscience and Petroleum, 7491 Trondheim, Norway.

biosynthesized together with other carotenoids ca. 3.5 billion years ago, Note S2 (Blankenship, 2010). Nevertheless, carotenoid acids are inadvertently or purposely ignored in textbooks and fatty acid inventories, such as the Lipid Handbook, the LipidBank database and other manuals and references. (Harwood et al., 2007; Nishijima, 2007; Kenar et al., 2017; Jie and Pasha, 1998; Twining et al., 2016) Carotenoid acids may have been overlooked, because lipids with such acids have not (yet) been detected in nature. The possible objection “only acids extracted from fats are rightfully called fatty acids” can, however, be repudiated. In the geochemical time frame, acids came first, fats later. (Szostak, 2017)

The attribute “surfactant” is determined by the amphiphilic character of the sodium and potassium salts, generally known as soaps and applied as detergents for over 4000 years. (Routh et al., 1996) In nutrition, saturated fats and fatty acids gained lately a rather unhealthy reputation at variance with the numerous putative benefits of unsaturated fats and fatty acids. In contrast to diet, cleaning with unsaturated fatty acid alkali salts came up only recently and hesitantly (Kawahara et al., 2012); saturated soaps stand all times strong and resolutely maintain the bathroom monopoly. Some alkali salts of mono or polyunsaturated fatty acids have been manufactured, but unsaturation is typically small and conjugation of double bonds is kept low (Kawahara et al., 2012). Salt formation accelerates decomposition, e.g. C8:3-Na and C10:4-Na easily autoxidize (Kuhn and Hoffer, 1930).

In *lipid (fat) synthesis*, fatty acids are typically esterified with hydroxypropane derivatives (glycerol, phosphatidyl glycerol, phosphatidyl choline).

1.2. Objectives

We aim to review in this paper the occurrence and synthesis of carotenoid acids presenting new details on the surface properties of alkali salts (Na, K, Cs) of these conjugated polyenoic methyl branched fatty acids. The critical micelle concentration c_M of carotenates will be associated with corresponding c_M -values of carboxylates. We further recapitulate esterification reactions of carotenoid acids with di- and triols to fats (glycol- and glycerolipids, glycerophospholipids). We highlight special applications engendered by the presence of conjugated polyene chains in fats. Finally, we make a plea for inclusion of carotenoid acids in fatty acid inventories.

2. Experimental

2.1. Carotenoid acids

The carotenoid acids, Fig. 1, were used as delivered or synthesized according to established procedures. Commercially available are acids C10:1, C12:2, C15:3 and in large amounts the industrially produced acids C20:5 and C30:9. C10:1 can be prepared by oxidation of β -cyclocitral with NaClO_2 (Wang et al., 2014; Dalcaneale, 1986). C12:2 was obtained by oxidation of β -ionone with NaOCl . (Royals, 1947; de Tribolet and Schinz, 1954) C15:3 ethylester was synthesized by a Reformatsky reaction of β -ionone with ethyl-2-bromoacetate (Karrer et al., 1932, 1946) The reported Reformatsky reaction of C17:4 gave low yields and was replaced by a Horner-Wadsworth-Emmons reaction, Note S3. Acids C20:5–C45:15 have been described previously (Zaidi et al., 2013). Several other syntheses of acid series C15:3–C22:6 and C20:5–C40:13 are known (Das and Becker, 1978; Wang et al., 2005).

C10:1 β -cyclogeranic acid, C12:2 cyclocitrylideneacetic acid, C15:3 β -ionylideneacetic acid, C17:4 β -ionylideneacetic acid, C20:5 retinoic acid, C22:6 retylideneacetic acid, C35:11 neurosporaxanthin, C40:13 torularhodin. C22:6 β -14'-apo-, C25:8 β -12'-apo-, C27:8 β -10'-apo-, C30:9 β -9'-apo-, C32:10 β -6'-apo-, C35:11 β -4'-apo-carotenoid acid. The characteristic polyene chain curving appears in the molecular structure of acids C20:5 – C45:15. (Martinez et al., 2018) A shade of yellow becomes visible with C17:4; the acids starting with C20:5 are

distinctly colored.

2.2. Carotenoid acids

C20:0 and C30:0 carotenoid acids, Fig. 2, were obtained as complementary saturated homologues of C20:5 and C30:9 acids by hydrogenation at 6 atm with Pt on charcoal, Note S4.

2.3. Alkali salts of carotenoid and carotenoid acids

Na and K salts of carotenoid and carotenoid acids were formed by dissolving the acids in MeOH adding MeOK or MeONa. Cs salts were obtained from a DCM solution of the acids with CsOH, Note S5.

2.4. Tensiometric measurements

Surface data were recorded with a Krüss Processor Tensiometer K100 with a Methrom 765 Dosimat addition pump. The set up was controlled by a Krüss Laboratory Desktop (version 3.1.0.2528). A Wilhelmy platinum plate was used for all measurements. Measurements and calculations are communicated in Notes S6–S8.

3. Results and discussion

3.1. Carotenoid acids

Acids C10:1, C12:2, C15:3, C20:5, C22:6, C25:7, C27:8, C30:9, C35:11 and C40:13 have been found in nature, Fig. 1 (Demole and Berthet, 1972; Eroglu et al., 2012). Spectroscopy and molecular structure of acids C20:5 – C45:15, color range of acids C20:5 – $C\infty:\infty$ and antioxidant properties have been described

previously. (Zaidi et al., 2013; Martinez et al., 2018) The UV–vis absorption of acids C10:1–C17:4 are commented in Note S9. Acid C45:15 represents probably not the limit in the series, which may be elongated with acids of much longer polyene chains (Zeeshan et al., 2012).

3.2. Surfactant properties of alkali carboxylates, carotenates and carotenates

The *critical micelle concentration* c_M , the concentration at which monomers of amphiphiles form aggregates (micelles), (Rosen and Kunjappu, 2012) is the key parameter of fatty acid salts and, consequently, was taken as a yardstick for characterizing the aggregation and surface behavior of Na, K and Cs salts of carboxylic acids, carotenoid and carotenoid acids, Figs. 1 and 2. The c_M of carboxylates are scrupulously enumerated; the listed c_M -values reflect diverse determination methods and varying accuracy; (Mukerjee and Mysels, 1971; Li et al., 2014) c_M decreases rapidly with the number of carbon atoms, Fig. S1; only linearly fitting valuations (linearized as $\ln c_M$) were selected from the c_M -compilation. (Mukerjee and Mysels, 1971) The critical micelle concentrations specified as $\ln c_M$ of Na-, K- and probably Cs-carboxylates C4:0 – C 18:0 are comparable, Note S7, Table S4 and Fig. S6. (Mukerjee and Mysels, 1971) Since surface properties of alkali carotenates and carotenates are not known, we determined c_M and related parameter by surface tension (γ) measurements, Notes S6 and S7. The elevated c_M of Na-carotenates compared to K-carotenates (C10:1–C17:4), Note S7, Tables S1–S3, and Fig. S7, express aggregate formation at higher concentration; Na-carotenates are, therefore, more hydrophilic than the analogous K-salts. Both Na- and K-carotenates aggregate at elevated c_M compared to the corresponding salts of the saturated acids.

It has been demonstrated previously by evaluating polyenic and saturated phospholipids that double bonds increase hydrophilicity. (Foss et al., 2005a) This effect could be confirmed by comparing Na-carotenates and Na-carboxylates: c_M of C10:1 is equivalent to c_M of

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