自動酸化マグロ肝油中の新規な共役カルボニルの同定

誌名	日本水産學會誌
ISSN	00215392
著者	濱, 洋一郎 中村, 孝
巻/号	54巻9号
掲載ページ	p. 1669-1669
発行年月	1988年9月

Short Paper

Identification of a New Conjugated Carbonyl in Autoxidized Tuna Liver Oil

Yoichiro Hama* and Takashi Nakamura*

(Received January 12, 1988)

In previous papers,[1,2] we reported that conjugated carbonyls with a hydroxypentanone ring, which were produced by autoxidation of polyunsaturated fatty acids with more than three double bounds, could form reddish pigments (λ_{max} 510–520 nm) when reacting with amino acids. The carbonyls, red pigment-forming substances (RPS), were purified from autoxidized linolenate, arachidonate and eicosapentaenoate, and their chemical structures were determined.[3–5] In autoxidized eicosapentaenoate, four out of six RPS predicted from the formation mechanism proposed for RPS[2,3] were present (Fig. 1, I-IV), but the remainder which have the side chains containing an active methylene group (Fig. 1, V, VI) could not be detected.[5] In this paper, we report the presence of one of them, 3-(5-hydroxy-2-octa-2,5-dienyl-3-oxocyclopentyl)-2-propenal (Fig. 1, V) in autoxidized tuna liver oil.

Triglycerides of tuna liver oil purified with activated carbon were oxidized at 40°C for 72 h in the dark (peroxide value 1200 meq/kg). The fatty acid composition of the triglycerides was as follows: $C_{16:0}$, 13%; $C_{18:1}$, 22%; $C_{20:1}$, 15%; $C_{22:1}$, 13%; $C_{20:5}$, 9%; $C_{22:6}$, 10%. Methods for preparation and identification of the RPS were the same as described[1–5]. Namely, the RPS produced were purified by gel chromatography on Sephadex LH-20 (Pharmacia Fine Chem. Co.) with $CHCl_3$/MeOH (2/1, v/v) as the eluent, and column chromatography on Silicagel 60 (E. Merck Co.) with $CHCl_3$/MeOH (97/3, v/v). After reduction with $NaBH_4$ or $NaBD_4$ and subsequent trimethylsilylation of the purified fraction, the RPS were analyzed by gas chromatography-mass spectrometry. By applying an electron impact mass spectrometry (the ion accelerating voltage, 1.5 kV; the ionizing voltage, 20 eV), two isomers (equivalent chain length 19.4, 19.7, determined using authentic fatty acid methyl esters[6]) of derivatized compound V in Fig. 1 were detected. Both fragmentation patterns were similar. A mass fragmentation of the trimethylsilyl (TMS) ether of the former obtained after reduction with $NaBH_4$ was as follows: m/z 392 (M-90, loss of HOTMS, 30%), 379 (M-103, loss of CH_2OTMS, 8), 377 (M-90–15, 6), 373 (M-109, loss of side chain, 5), 366 (M-116, loss of C_2H_3OTMS, 3), 355 (4), 341 (3), 323 (11), 302 (M-180, 42), 297 (9), 289 (13), 283 (M-90–109, 14), 276 (M-90–116, 16), 263 [M-219, loss of $C_3H_5(OTMS)_2$, 22], 257 (M-116–109, 100), 247 (12), 243 [$C_5H_5(OTMS)_2$, 16], 233 (25), 223 (14), 219 (50), 217 [$C_8H_3(OTMS)_2$, 60], 212 (16), 207 (33), 197 (16), 191 [$CH(OTMS)_2$ 55], 186 (19), 183 (20), 173 (16), 171 (14), 167 (C_6H_6OTMS, 60), 155 (31), 149 (19), 147 (19), 144 (29), 143 (31), 131 (34), 129 (55), 117 (36), 108 (23) and 103 (55). The fragment ions m/z 191, 217 and 243 are common to TMS ethers of the dihydroxypentane ring, as of the prostaglandin F groups.[7] The ions m/z 167, M-219, M-206, 257, 283 and 373 are characteristic for the TMS derivatives of RPS.[2–5] These fragmentations also indicated the molecular size of the side chain other than 2-propenal; C_3H_{13} 109. The fragment ions containing deuterium obtained after $NaBD_4$-reduction suggest the position of carbonyl groups in the mother compound as described in previous papers.[3–5] Thus, the compound is assigned as the TMS derivative of 3-(5-hydroxy-2-octa-2,5-dienyl-3-oxocyclopentyl)-2-propenal. In addition, the RPS already identified[2,5] (Fig. 1, I, III) were also found in this study. Quantitative estimation using mass fragmentography showed formation of 0.05% total RPS containing 0.01% RPS (V) in the autoxidized tuna liver oil.

References

1) T. Nakamura: *Nippon Suisan Gakkaishi*, **50**, 477–479 (1984).
2) T. Nakamura: *Lipids*, **20**, 180–186 (1985).
3) T. Nakamura: *Lipids*, **21**, 553–557 (1986).
4) T. Nakamura and Y. Hama: *J. Agr. Food Chem.*, **36**, 15–18 (1988).
5) T. Nakamura and Y. Hama: *Nippon Suisan Gakkaishi*, **54**, 271–275 (1988).
6) J. J. Mayer: in "Fatty Acids and Glycerides" (ed. by A. Kuksis), Plenum Press, New York and London, 1978, p 144.
7) M. Hamberg and V. J. Israelsson: *J. Biol. Chem.*, **245**, 5107–5114 (1970).

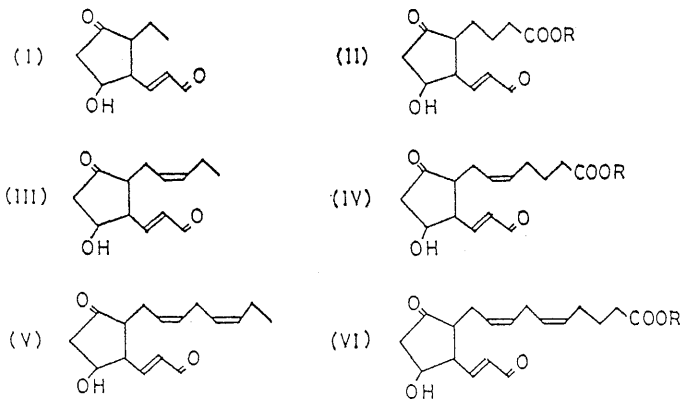

Fig. 1. Red pigment-forming substances predicted in autoxidized eicosapentaenoate

* Laboratory of Fisheries Technology, Faculty of Agriculture, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan (濱 洋一郎, 中村 孝: 九州大学農学部水産化学第二教室).

Nippon Suisan Gakkaishi : Formerly *Bull. Japan. Soc. Sci. Fish.*