Synthesis of Traumatic Half Aldehyde and Related Compounds

Tadahiko KAJIWARA, Jiro SEKIYA, Yasuji KIDO and Akikazu HATANAKA

Department of Agricultural Chemistry, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753, Japan

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We have proposed the biosynthetic pathway of C9-unsaturated aldehyde, (E)-2-hexenal (leaf aldehyde) and C12-oxo-unsaturated acid, (E)-11-formyl-10-undecenoic acid (traumatic haldehyde) in chloroplasts of tea leaves.1-10

The formation of C9-aldehyde, leaf aldehyde, via (Z)-3-hexenal from linolenic acid was elucidated by a tracer experiment with linolenic acid-[U-14C].7 However, the formation of C12-oxo-acid, traumatic hal aldehyde, via (Z)-11-formyl-9-undecenoic acid was not explored. In this connection of studies on the occurrence of C12-oxo-acids in the chloroplasts, the work leading to synthesis of traumatic hal aldehyde and the related compounds was stimulated.

This paper describes stereoselective synthesis of methyl (Z)-11-formyl-9-undecenoate (1-a), methyl (E)-11-formyl-10-undecenoate (1-b).

With P-2 Ni prepared from nickel acetate and sodium borohydride, methyl 12-hydroxy-9-dodecenoyl and methyl 12-hydroxy-10-dodecenoyl prepared by the procedure of Ames11) were semi-hydrogenated in ethanol or methanol containing a small amount of ethylenediamine to the desired sterically pure methyl (Z)-12-hydroxy-9-dodecanoate (2-a) and methyl (Z)-12-hydroxy-10-dodecanoate (2-b) in nearly quantitative yields.

The (Z)-12-hydroxy-9-unsaturated ester (2-a) was oxidized with pyridinium chlorochromate, C6H5-NHCrO3Cl,11) to the corresponding oxo-ester (1-a) with considerable amounts of α, β-unsaturated isomer and other contaminants. However, the desired methyl (Z)-11-formyl-9-undecenoate (1-a) was obtained by oxidation of (2-a) with CrO3-pyridine complex in dichloromethane without isomerization to α, β-E-conjugation.4,10 Methyl (E)-11-formyl-10-undecenoate (1-b) also was obtained by oxidation of (2-b) under similar condition in satisfactory yield. The structure of C12-oxo-acid esters (1-a and b) thus obtained were fully established by IR and NMR spectra. The occurrence of traumatic hal aldehyde and (Z)-11-formyl-9-undecenoic acid in chloroplasts of tea leaves was first confirmed by comparison of GLC retention times with synthetic specimens (1-a and b). The enzymatic formation of traumatic hal aldehyde via (Z)-11-formyl-9-isomer from linolenic acid in the chloroplasts was clarified using a 14C-labelling technique with linolenic acid-[1-14C] as shown in Scheme 1.14

EXPERIMENTAL

IR spectra were obtained by Hitachi EPI-G2 spectrometer using sodium chloride disk. NMR spectra were taken with a Hitachi Perkin-Elmer R-24 spectrometer at 60 MHz with TMS as an internal standard. MS spectra were taken on a Japan spectroscopic Model TAM-05G spectrometer. GLC was carried out on a Shimadzu Chromatography Model GC-4B or GC-1C.

Methyl (Z)-12-hydroxy-9-dodecenoate (2-a)

The nickel acetate (1.36 g: 5.4 mmol) was dissolved in dry methanol (70 ml). After the injection of sodium borohydride (207 mg: 5.45 mmol) in dry methanol to the rapidly stirred solution of nickel acetate, ethylene diamine (1 ml) was added.15,16) Hydrogenation was then initiated by introducing methyl 12-hydroxy-9-dodecenoate (1.16 g: 5.46 mmol). After the absorption of calculated amount of hydrogen (5.5 mmol), the reaction mixture was filtered and isolated with ether. Solvent-free oil was distilled to give (Z)-12-hydroxy-unsaturated ester (2-a, 801 mg: 68%) at 139-142°C (0.25 mmHg), IR νmax cm\(^{-1}\): 3400, 1740, 1050.

Methyl (Z)-11-formyl-9-undecenoate (1-a)

Chromium trioxide (3.0 g: 30 mmol) was added to magnetically stirred solution of pyridine (4.8 g: 61 mmol) in methylene chloride (75 ml). The solution was stirred for 15 min at room temperature and a solution of methyl (Z)-12-hydroxy-9-dodecenoate (2-a, 0.75 g: 3.5 mmol) in a small volume of methylene chloride was added in one portion. After an additional 15 min stirring at room temperature, the mixture was eluted through the silica gel with ether and eluate was washed by water, dried and distilled to give (Z)-11-formyl-9-unsaturated ester (1-a, 0.42 g: 57%) at 126-131°C (0.23 mmHg), IR νmax cm\(^{-1}\): 2700, 1730, 730. MS m/e: 226 (M+). 2, 4-DNPH; NMR (CCl\(_4\)) \(δ\): 10.9 (1H, s), 8.85 (1H, s), 8.12 (1H, d, \(J = 9.5\) Hz), 7.78 (1H, d, \(J = 9.5\) Hz), 7.37 (1H, m), 5.38 (1H, m), 3.48 (3H, s), 3.0 (2H, m), 2.03 (4H, m), 1.2 (10H, s).

Methyl (Z)-12-hydroxy-10-dodecenoate (2-b)

According to the method described in synthesis of methyl (Z)-12-hydroxy-9-dodecenoate, methyl (Z)-12-hydroxy-10-dodecenoate was prepared by hydrogenation of methyl 12-hydroxy-10-dodecenoate with P-2 Ni. The product was purified with distillation (bp
SCHEME 1. Biosynthetic Pathway of Leaf Aldehyde.

138～141°C (0.12 mmHg), 42%, IR $\nu_{\text{lim}}^{\text{max}}$ cm$^{-1}$: 3400, 1740, 1030. NMR (CCl$_4$): $\delta$ 5.42 (2H, m), 4.03 (2H, m), 3.57 (3H, s), 2.18 (4H, m), 1.8 (1H, -OH), 1.30 (12H, s).

Methyl (E)-11-formyl-10-undecenoate (1-b)

Methyl (Z)-12-hydroxy-10-dodecenoate (2-b) was oxidized with CrO$_3$-pyridine complex$^{(3)}$ or pyridinium chlorochromate$^{(3)}$ to give (E)-11-formyl-10-unsaturated ester (1-b) at 70% and 68%, respectively. IR $\nu_{\text{lim}}^{\text{max}}$ cm$^{-1}$: 1740, 1690. MS $m/e$: 226 (M$^+$). 2, 4-DNPH: NMR (CCl$_4$): $\delta$ 6.2 (2H, m), 3.5 (3H, s), 2.1 (4H, m), 1.23 (12H, s).

REFERENCES

1) A. Hatanaka and T. Harada, Phytochemistry, 12, 2341 (1973).