Note

 C_{15} and C_{17} Aldehydes, from Japanese Domestic Tobacco, *Nicotiana tabacum* cv. SuifuYoshikazu TAKAGI, Takane FUJIMORI,
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A large number of the volatile flavor constituents of tobacco have been thought to be generated by oxidative degradation of terpenoids such as carotenoids and thunberganoids during maturing and post-harvested treatment.^{1,2)} In the course of examination of the flavor constituents of Japanese domestic tobacco (*N. tabacum* cv. Suifu), we have isolated a C_{15} saturated and two C_{17} unsaturated fatty aldehydes from the neutral volatiles of green leaves at flowering time (just after topping). In this paper we report the isolation of these three aldehydes which could not be detected in aged tobacco leaves.

Twenty grams of dry weight of Suifu tobacco at

flowering time were steam distilled and neutral volatiles were extracted from the distillate. Compound A, B and C were isolated from the neutral volatiles by column chromatography on a silicic acid column (*n*-hexane: Et_2O = 1:1) followed by preparative gas liquid chromatography (2.5 mm $\times$ 1 m glass column, 5% FFAP on Chromosorb W, He flow 50 ml/min), as shown in Fig. 1.

Compound A Compound A was isolated as 10 mg of a colorless oil. The mass spectrum showed significant peaks at m/z 248 (M^+ , 1.3%), 192 (4), 135 (4), 121 (13), 108 (36), 95 (45), 93 (47), 91 (30), 79 (100), 67 (81) and 55 (56). In the IR spectrum, bands were showed at 3200 cm^{-1} (s), 2935 (s), 2855 (s), 2710 (s, $-CHO$), 1728 (s, $C=O$), 1460 (s), 1382 (m), 1267 (m), 1066 (m) and 715 (s, $Z-CH=CH-$), but no band of (*E*) disubstituted double bond in the $960\sim980\text{ cm}^{-1}$ region indicating an aliphatic aldehyde with (*Z*) double bond. The mass and IR spectra were consistent with a C_{17} aldehyde containing three double bonds. The NMR spectrum (100 MHz, $CDCl_3$) showed a $-CHO$ group (δ 9.73, 1H, t, $J=1.7$ Hz), three $-CH=CH-$ groups (δ 5.33, 6H, m), two $-CH=CH-CH_2-CH=CH-$ groups (δ 2.64, 4H, t, $J=5.7$ Hz), a $-CH_2-CHO$ group (δ 2.30, 2H, t $\times$ d, $J=1.7$ and 6.9 Hz), two $=CH-CH_2-$ groups (δ 1.96, 4H, m) and a methyl group (δ 0.87, 3H, t, $J=7.3$ Hz). The resonance at δ 2.64 of 4H indicated that compound A had a partial structure, $-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$. Since irradiation at the triplet at δ 0.87 simplified the multiplet at δ 1.96, it followed that com-

FIG. 1. Gas Chromatogram of Neutral Volatiles of Suifu Tobacco at Flowering Time.

Conditions: column, FFAP 5% on Chromosorb W, 2.5 mm $\times$ 1 m; oven temp., $100\sim270^\circ\text{C}$ ($8^\circ\text{C}/\text{min}$); carrier gas, He, 50 ml/min; injection and detector temp., 280°C .

pound **A** had a terminal structure $\text{CH}_3\text{-CH}_2\text{-CH=}$ which established the position of the terminal double bond at carbon 14 and the remaining double bonds are located at carbons 11 and 8. Therefore, based on above spectral data and $^1\text{H}(^1\text{H})$ decoupling experiment, we identified compound **A** as (Z, Z, Z)-8,11,14-heptadecatrienal. These spectroscopic data of compound **A** were identical with those of (Z, Z, Z)-8,11,14-heptadecatrienal which had been isolated only from an aqueous cucumber homogenate.³⁾

Compound B Compound **B** (2.0 mg) eluted prior to compound **A** on FFAP column and yielded a mass spectral M^+ peak at m/z 250 (11%) and other major peaks at m/z 222 (2), 152 (3), 109 (22), 98 (28), 96 (27), 95 (49), 82 (30), 81 (70), 79 (38), 67 (100), 55 (51), 54 (42) and 42 (52). The IR spectrum showed bands at 3025 (s), 2940 (s), 2865 (s), 1730 (s, C=O), 2730 (m, -CHO), 1460 (m), 1380 (m), 1260 (m) and 715 (m, -CH=CH-), indicating an aliphatic aldehyde with (Z) double bond in analogy with compound **A**. The mass and IR spectra were consistent with a C_{17} aldehyde containing two double bonds. The NMR spectrum showed a -CHO group (δ 9.66, 1H, t, $J=1.7$ Hz), two -CH=CH- groups (δ 5.27, 4H, m), a -CH=CH-CH₂-CH=CH- group (δ 2.67, 2H, t, $J=5.4$ Hz), a -CH₂-CH₂-CHO group (δ 2.32, 2H, t x d, $J=1.7$ and 6.9 Hz), two =CH-CH₂- groups (δ 1.95, 4H, m), five -CH₂- groups (δ 1.22, 10H, m) and methyl group (δ 0.80, 3H, t, $J=5.6$ Hz). The resonance at δ 2.67 indicated that the double bonds were separated by a methylene group (analogous to results obtained with compound **A**). The mass fragmentation from a molecule, showing fragments at m/z 221, 207, 193, 165, 151 and 137, showed it possible that compound **B** was either (Z, Z)-8,11- or (Z, Z)-5,8-heptadecadienal. Above spectroscopic data of compound **B** agreed with those of (Z, Z)-8,11-heptadecadienal, which had been isolated only from an aqueous cucumber homogenate similarly to compound **A**.³⁾ Therefore, we identified compound **B** as (Z, Z)-8,11-heptadecadienal.

Compound C Compound **C** (a colorless oil, 2.5 mg) eluted prior to both compound **A** and **B** and the mass spectrum of compound **C** showed significant peaks at m/z

226 (M^+ , 0.5%), 208 (3), 182 (9), 180 (8), 152 (5), 138 (8), 122 (11), 110 (17), 109 (18), 96 (62), 83 (60), 82 (95), 81 (48), 71 (47), 69 (58), 68 (63), 67 (50), 57 (100) and 55 (79). The IR spectrum showed bands at 2940 cm^{-1} (s), 2870 (s), 2737 (m, -CHO), 1735 (s, C=O), 1470 (s), 1390 (m) and 670 (s). The mass and IR spectra were consistent with a C_{15} aliphatic aldehyde. The NMR spectrum showed a -CHO group (δ 9.67, 1H, t, $J=1.7$ Hz), a -CH₂-CH₂-CHO group (δ 2.32, 2H, t x d, $J=1.7$ and 7.1 Hz), -CH₂- groups (δ 1.17, ca. 24H, m) and a methyl group (δ 1.80, 3H, t, $J=6.9$ Hz). These spectroscopic data of compound **C** agreed with those of pentadecanal which had been isolated from cucumber.^{4,5)}

Compound **A** and **B** bear a structural relationship to the common C_{18} unsaturated fatty acid; linolenic acid and linoleic acid, and compound **C** would be related to C_{16} saturated fatty acid; hexadecanoic acid. In the case of cucumber, these fatty aldehydes would be formed when tissue was homogenated or ruptured.³⁾ In this experiment, tobacco leaves were immediately frozen to -20°C just after harvesting but it required further examination to confirm when these fatty aldehydes were formed in tobacco leaves.

On the other hand, the vaporous products of fatty acid degradation in tobacco leaves have been known to be reduced during post-harvest treatment.¹⁾ The contents of compound **A**, **B** and **C** were decreased to ca. 1/4, ca. 1/2 and ca. 1/2 during maturing and they could not be detected just after drying.

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