Isolation of R-(—)-3-Hydroxy- β -ionone from Burley TobaccoTakane FUJIMORI, Reiko KASUGA,
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It is generally considered that a large number of flavoring constituents in tobacco is closely related to the metabolites or the degradation products of carotenoids, diterpenes, and nicotine.¹⁾

In this communication, we wish to report the isolation of a new keto-alcohol, R-(—)-3-hydroxy- β -ionone (I), which is also considered to be a degradation product of carotenoids.

The fraction bp 29~96°C/0.002 mmHg (248.5 g), designated as 'M-fraction,' in neutral oil of Burley tobacco was obtained from 370 kg of air-cured Burley leaves by means of dichloromethane extraction, steam-distillation, fractionation, and distillation. Repeated silica gel column chromatography and silica gel thin-layer chromatography of the M-fraction gave a fraction M-18-10-5. A gas chromatogram of this fraction is shown in Fig. 1.

FIG. 1. Gas Chromatogram of Fraction-M-18-10-5. Conditions; Column: 10% PEG 20M on Chromosorb W, 3 mm $\times$ 2 m. Temp.: Programming from 100°C to 240°C at 5°C/min. Carrier Gas: 2 kg He/cm².

P-A and P-B (6 mg) in Fig. 1 were obtained as fragrant liquids by preparative gas chromatography of M-18-10-5. By mass and infrared spectra, P-A was assigned as 3-hydroxy- β -damascone which had been reported as a flavoring component of Manila tobacco.²⁾

In a high resolution mass spectrum, P-B showed the molecular ion at m/e 208.149; hence the molecular formula of the compound was estimated as C₁₃H₂₀O₂ (Calcd.: 208.146).

The infrared spectrum bands at 3400 and 1670 cm⁻¹ suggested a hydroxy group and α,β -unsaturated ketone, respectively.

In the UV spectrum, two absorption bands at 222 nm and 291 nm suggested a conjugated dienone structure.

The NMR signals (Table I) had strong resemblance to those of β -ionone except the 1H multiplet at δ 3.95 which showed the structure of -CH-.

TABLE I. SPECTRAL DATA OF P-B

MS m/e	208 (M ⁺) 193 (100%) 190 175 43	IR	3400 cm ⁻¹ 1670 1606 1362 1255 1172
UV $\lambda_{\text{EtOH}}^{\text{max}}$	222 nm (ϵ =6150) 291 (ϵ =7200)		1050 978
NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$	1.10 (s, 6H) 1.76 (s, 3H) 2.28 (s, 3H) 3.95 (m, 1H) 6.08 (d, 1H, J =16.6 Hz) 7.14 (d, 1H, J =16.6 Hz)	$\text{>C(CH}_3)_2$ >C=C-CH_3 -CO-CH_3 -CH(OH)- -CH=CH-CO- -CH-CH-CO-	

Based on these data, P-B was presumed as 3-hydroxy- β -ionone (4-(4-hydroxy-2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one).

3-Hydroxy- β -ionone has been synthesized by D. E. Loeber *et al.*³⁾ The spectroscopic data of P-B were identical with those of the synthetic one.

P-B had a specific rotation of $[\alpha]_D^{20} -77.9^\circ$

($c=0.010$, CHCl_3). Recently, K. Mori established the absolute configuration of (—)-3-hydroxy- β -ionone as (I) by synthetic method.⁴⁾ Hence, the natural (—)-3-hydroxy- β -ionone has R-configuration as to its asymmetric center.

With respect to the configuration of hydroxy group, the natural (I) has the same configuration as zeaxanthin.⁵⁾ This fact supports the assumption that (I) is formed by oxydative degradation of carotenoids such as zeaxanthin which has 3-hydroxy group.

This is the first report which shows natural occurrence of R-(—)-3-hydroxy- β -ionone.

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