Short Communication

Isolation of 8,9-Dehydrotheaspirone
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The essential oil of cured tobacco leaves is known to contain more than eighty carotenoid-related aroma compounds.¹⁾ Of these compounds, theaspirone²⁾ and 2,6,6,10-tetramethyl-1-oxaspiro[4.5]dec-2-ene-8-one³⁾ have been isolated as compounds having a spiro structure. Theaspirone was originally reported as an important component of tea aroma²⁾ and the synthesis of this compound has been done by several methods.^{4~8)}

In this communication, we wish to report the isolation of a new spiro compound related to theaspirone from air-cured American Burley tobacco leaves (*Nicotiana tabacum* cv. Burley). Fraction M-17 in a previous paper⁹⁾ (100% ether eluate through a silicic acid column) was rechromatographed on a silicic acid column in twenty-two portions with a benzene-ethyl acetate solvent system. Preparative GLC (5% FFAP, 1 m) of Fraction M-17-14 eluted with 30% ethyl acetate gave compound **1** (5 mg) as an oil. The isolated **1** had a strong flowery-woody odor.

The GC-FI mass spectrum (Hitachi M-80 mass spectrometer, 5% FFAP, 1 m) of **1** showed a molecular ion at m/z 206. EI-MS showed significant peaks at m/z 206 (M^+ , 19%), 191 (6), 150 (27), 136 (14), 121 (10), 108 (65), 93 (33) and 43 (100). By high resolution MS, the formula of **1** was determined to be $C_{13}H_{18}O_2$ (found: 206.1326, calcd.: 206.1306). The IR spectrum showed an α,β -unsaturated carbonyl group at 1670 cm^{-1} . No hydroxyl group was observed. The UV spectrum show-

ed an absorption band at 235 nm ($\epsilon=5450$) which was consistent with an enone system. The $^1\text{H-NMR}$ spectrum (100 MHz, CDCl_3) showed *gem*-dimethyls (δ 1.00, 3H, s; δ 1.08, 3H, s), a methyl group attached to the β -position of an α,β -unsaturated carbonyl group (δ 1.96, 3H, d, $J=1\text{ Hz}$), a methyl group of the α -position of an enol ether group (δ 1.80, 3H, br s), a methylene group adjacent to a double bond (δ 2.45, 1H, dd, $J=16$ and 2 Hz; δ 3.04, 1H, dd, $J=16$ and 2 Hz), a methylene group adjacent to a carbonyl group (δ 2.16, 1H, d, $J=16\text{ Hz}$; δ 2.43, 1H, d, $J=16\text{ Hz}$), a methine of a double bond (δ 4.51, 1H, m) and a methine of the α -position of an α,β -unsaturated carbonyl group (δ 5.67, 1H, s). These spectral data indicated that compound **1** was 8,9-dehydrotheaspirone, 2,6,10,10-tetramethyl-1-oxaspiro[4.5]deca-2,6-diene-8-one.

The structure of the isolated **1** was further confirmed by a synthesis. 8,9-Dehydrotheaspirone was produced from synthetic blumenol B by oxidation with pyridinium chlorochromate in ethyl acetate solution at room temperature. The spectral data of the isolated **1** were all identical with those of the synthetic 8,9 dehydrotheaspirone.

Compound **1** was not so stable and was partially converted to the ketol **2** in chloroform at room temperature. GLC of **1** and **2** showed retention times of 7.2 min and 9.9 min, respectively (5% OV-101, 1 m, programmed from 100° to 240° at $10^\circ/\text{min}$). Mass and $^1\text{H-NMR}$ spectra of **2** were as follows; MS m/z : 224 (M^+ , not discernible), 206 (5), 168 (31), 150 (11), 111 (100), 108 (18), 93 (33) and 43 (92), $^1\text{H-NMR}$ (CDCl_3) δ : 0.99 (3H, s), 1.02 (3H, s), 2.09 (3H, s) and 5.81 (1H, s). Treatment of **2** with *dil*- H_2SO_4 in chloroform gave compound **1** easily.

Compound **1** was also present in the volatiles¹⁰⁾ of Japanese domestic Suifu tobacco leaves.

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