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A NEW ACETYLENIC DIOL, 3-HYDROXY-7,8-DEHYDRO-β-IONOL, FROM BURLEY *NICOTIANA TABACUM*

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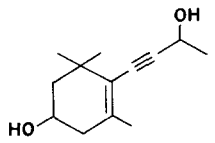
In a recent publication, the occurrence of 3-hydroxy-β-ionone [1] which is considered to be a degradation product of carotenoids such as zeaxanthin and lutein was reported in the neutral volatile constituents of Burley tobacco (*Nicotiana tabacum* L.). We wish to report here the isolation of a novel enyne alcohol, 3-hydroxy-7,8-dehydro-β-ionol **(1)**, which is also considered to be a degradation product of carotenoids.



(1)

The fraction, bp 29 ~ 96°C/0·002 mm Hg (248·5 g), designated as "M-fraction", in the neutral oil of Burley tobacco was obtained from 370 kg of air-cured Burley tobacco leaves by means of dichloromethane extraction, steam-distillation, fractionation and distillation. Repeated silicic acid column chromatography and preparative GLC gave pure **(1)** {$[\alpha]_D^{17}$ −82·6° (EtOH; *c* 0·27)} in a 0·02% yield based on the total M-fraction. This substance has a strong floral fragrance. The MS showed peaks at *m/e* 208 (M^+), 193, 190, 175, 131, 105, 91 and 43. By high resolution MS, its formula of **(1)** was estimated as $C_{13}H_{20}O_2$ (found: 208·1463, calcd.: 208·1444). The NMR spectrum (100 MHz, $CDCl_3$) showed an allylic geminal dimethyl group (δ1·12, *s*, 3H; δ1·18, *s*, 3H), an olefinic methyl group (δ1·90, *s*, 3H), a methyl group attached to a carbinol carbon (δ1·52, *d*, *J* 7·0 Hz, 3H), two carbinol methines (δ3·98, *m*, 1H; δ4·72, *q*, *J* 7·0 Hz, 1H) and hydroxyl groups (δ1·86, *s*, 2H, exchangeable with D_2O). In a double resonance experiment with irradiation at δ4·72, the doublet at δ1·52 changed to a singlet. No olefinic proton was observed in the NMR spectrum. The IR spectrum showed hydroxyl groups at 3350 cm^{-1}, a geminal dimethyl group at 1360 and 1375 cm^{-1} and an acetylenic linkage at 2200 cm^{-1}. No carbonyl group was observed. The UV spectrum had λ_{max}^{EtOH} 230·5 nm (ε 12700) which was consistent with a conjugate system.

On the basis of the data outlined above, **(1)** was identified as 4-(4-hydroxy-2,6,6-trimethylcyclohex-1-enyl)but-3-yn-2-ol. This compound has been prepared as an intermediate in the synthesis of zeaxanthin and other xanthophylls [2]. The spectral data of the isolated **(1)** were identical with those of the synthetic compound.

This is the first report of the occurrence of an acetylenic carotenoid-like compound in tobacco or other higher plant although several acetylenic carotenoids such as alloxanthin [3] have been isolated from algae. The isolation of **(1)** suggests that acetylenic carotenoids themselves may be found in higher plants, since ionones and related compounds are considered to be the degradation products of carotenoids.

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