Isolation of 3-(4,8,12-Trimethyltridecyl)-furan ("Phytofuran") from Burley Tobacco

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In this communication, we wish to report the isolation of a diterpene furan, 3-(4,8,12-trimethyltridecyl)-furan ("Phytofuran") (I), from Burely tobacco.

A fraction bp 29~96°C/0.002mmHg(248.5g), designated as 'M-fraction,' in the neutral oil of Burley tobacco was obtained from 370 kg of air-cured Burley leaves.¹⁾ A 2:98 ether-*n*-hexane eluate from a silicic acid column chromatography of M-fraction was designated as M-2 fraction (2.7 g). P-A and P-B in Fig. 1 were obtained by preparative gas chromatography of M-2. By mass and infrared spectra, P-A was assigned as neophytadiene (γ -phytadiene).^{2,3)}

FIG. 1. Gas Chromatogram of M-2.

Conditions; Column: 10% Silicone SE-30 on Dia-solid L, 3 mm×3 m. Temp.: Programming from 100°C to 250°C at 5°C/min. Carrier Gas: 2 kg He/cm².

In the mass spectrum, P-B showed the parent ion at *m/e* 292 and the base peak at *m/e* 82.

The infrared spectrum showed the presence

of three bands at 1500, 873 and 780 cm⁻¹ which were characteristic of furans.

A high resolution mass spectrometry gave the elementary composition of the *m/e* 292 peak as C₂₀H₃₈O (Found.: 292.273, Calcd.: 292.277) and that of the base peak of *m/e* as C₈H₆O (Found.: 82.047, Calcd.: 82.042).

The NMR signals at δ 6.15(1H), δ 7.10(1H) and δ 7.23 (1H) corresponded to a furan structure. These three signals suggested a structure of $\begin{array}{c} \text{C} - \text{C} - \text{R} \\ \parallel \quad \parallel \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$.

NMR signals had a strong similarity to that of neophytadiene.

From these spectral data, the structure of P-B was assigned as 3-(4,8,12-trimethyltridecyl)-furan (I).

To prepare (I), a dye-sensitized photo-oxygenation of neophytadiene was carried out according to the procedure of E. Demole *et al.*⁴⁾ A solution of 50 mg (0.18 mmole) of gas chromatographically pure neophytadiene and 50 mg of Rose Bengal in 350 ml of benzene was irradiated by a high pressure mercury lamp for 6 hr at 25°C in the presence of a constant flow of dry oxygen (150 ml/min). An aliquot of the reaction mixture was directly injected into a gas chromatograph. The expected furan was obtained in an 8% yield.

The spectral data of the isolated sample were all identical with those of the synthetic one.

Recently, solanofuran was isolated from Burley tobacco and was synthesized by photo-oxygenation of solanone by E. Demole *et al.*⁴⁾ They considered it to be a solanone metabolite which probably arised from photo-oxygenation of the ketone during the aerobic treatment of the tobacco leaves.

Phytofuran also seems to be arisen from photo-oxygenation of neophytadiene. The occurrence of this furan may support the view⁴⁾ that certain naturally occurring terpenoid furans are formed from their conjugated diene pre-

cursors.

The details of this paper will be published later.

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