data indicate its similarity with myricetin,[16] absence of any shift in the Band II of the UV spectrum on addition of anhydrous sodium acetate indicates absence of free hydroxyl at C-7.

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Key Word Index—Madhuca longifolia, Sapotaceae, erythrodiol caproate, oleanolic palmitate, triterpenoid esters, Sapotaceae.

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SOLANACEAE

BOMBIPRENONE FROM *NICOTIANA TABACUM*

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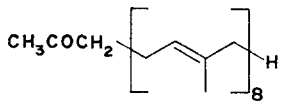
Abstract—Bombiprenone (6,10,14,18,22,26,30,34-octamethyl-5,9,13,17,21,25,29,33-pentatriacontaoctaen-2-one) has been isolated from flue-cured tobacco (*Nicotiana tabacum*) in yields of 0 1–0 6% dry wt. Plastoquinone-A was converted to bombiprenone by aerobic photo-oxidation, most probably via a hydroperoxide

A LIPID component isolated from flue-cured tobacco by a procedure involving hexane extraction, column chromatography on Florisil, and preparative-layer chromatography on silica gel G has been identified as 6,10,14,18,22,26,30,34-octamethyl-5,9,13,17,21,25,29,33-pentatriacontaoctaen-2-one (I)



(I)

In 1960, Kofler *et al.*[1] prepared (I) as an intermediate for the total synthesis of solanesol Eight years later, (I) was isolated in 0·4% yield from the unsaponifiable matter obtained from the lipid extract of the faeces of the silkworm (*Bombyx mori*, L) by Toyoda *et al*[2] who proposed the trivial name bombiprenone Bombiprenone was also isolated in 0·002% yield from the leaves of mulberry (*Morus bombycis*, K.), which is the sole diet of the silkworm

[1] R RUEGG, U GLOOR, A LANGEMANN, M KOFLER, C VON PLANTA, G RYSER and O ISLER, *Helv. Chim Acta* **43**, 1745 (1960)
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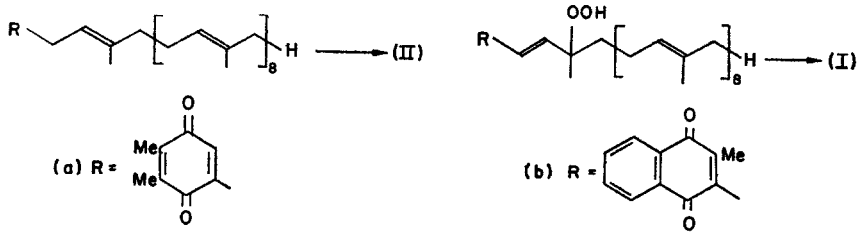
Bombiprenone was easily detected on TLC giving a distinctive yellowish–green colouration with anisaldehyde/sulphuric acid spray reagent [3] The mass spectrum showed a molecular ion $m/e = 602$ and the fragmentation pattern confirmed the structure (I) showing the loss of a terminal isoprene unit ($m/e = 69$) followed by successive loss of seven further isoprene residues ($m/e = 68$) from the ω-end leaving a residual fragment $m/e = 57$ The IR spectrum exhibited strong carbonyl absorption at 1720 cm^{-1}. The NMR spectrum was in agreement with that reported by Toyoda [2]

TLC examination of hexane solutions of plastoquinone-A (II), which had been allowed to stand at room temp for several days or which had been infused with oxygen for several hours showed that decomposition had occurred to give bombiprenone Snyder and Rapoport[4] have reported the formation of bombiprenone by the aerobic photo-oxidation of menaquinone-45 (III) and the following mechanism was proposed



It is suggested, therefore, that plastoquinone-A, the most abundant nonaprenylquinone in *Nicotiana tabacum*,[5] yields bombiprenone by a similar mechanism after the death of the plant when it no longer has to fulfil its role in photosynthesis

Thin-layer densitometric analysis of the hexane extracts of samples of flue-cured tobacco has shown that the amounts of bombiprenone present varied between 0 1–0 6 dry wt

EXPERIMENTAL

The UV spectrum was recorded in EtOH, the NMR spectrum in $CDCl_3$ at 60 MHz and the IR spectrum as a thin film between NaCl discs The MS was determined on the A E I MS 12 instrument C S chambers were used for TLC

Extraction and characterization of bombiprenone The concentrated light petroleum (b p 30–40°) extract of ground, flue-cured tobacco (140 g) was chromatographed on Florisil The concentrated Et_2O/hexane eluate containing bombiprenone was twice subjected to preparative-TLC on silica gel G (2 mm) plates in light petroleum (b p 60–80°)/Et_2O (9 1) TLC was carried out on silica gel G (0 25 mm) plates which were sprayed with anisaldehyde/H_2SO_4 (5 ml anisaldehyde 5 ml c H_2SO_4/90 ml 90% EtOH) and heated for 2 min at 110° to develop the characteristic yellowish–green colour, R_f in (A) $CHCl_3$ = 0 50, (B) benzene–EtOAc (4 1) = 0 50, (C) light petroleum–Et_2O (9 1) = 0 21 NMR spectrum δ 5 15 (C=CH), 2 4 (—CH_2 CO), 2 2 (MeCo—), 2 0 (—CH_2—), 1 65 ppm (C—Me), UV max (EtOH) 212 nm The principal features of the IR and mass spectra are described above

Densitometry Tobacco extracts (*ca* 500 μg) were chromatographed alongside bombiprenone standards on silica gel G in solvent system (C) followed by treatment with anisaldehyde spray reagent Densitometry was carried out using a Chromoscan densitometer with a TLC attachment operating in the reflectance mode A violet filter was placed in the sample beam to obtain maximum sensitivity The bombiprenone content of the samples was calculated from the calibration curve obtained for the standards (peak area vs amount of bombiprenone)

[3] G P McSweeney, *J Chromatog* **17**, 183 (1965)
[4] C D Snyder and J Rapoport, *J Am Chem Soc* **91**, 731 (1969)
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Key Word Index—*Nicotiana tabacum*, Solanaceae, flue-cured tobacco, polyterpene, bombiprenone

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ALKALOIDS OF *SALPICHROA ORIGANIFOLIA*

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(*Received* 18 *August* 1971)

Plant Salpichroa origanifolia (Lam.) Baillon. [*S rhomboidea* (Hook.) Miers] *Uses and properties.* No known uses. Excessive consumption of fruit reported[1] to produce symptoms of drunkenness *Previous work.* Unnamed alkaloids.[1,2]

Root. Powdered root (20 g) with $Ca(OH)_2$ (4 g) and H_2O (6 ml); exhausted with ether (700 ml) Basic extract fractionated on kieselguhr supporting phosphate buffer solution pH 6 8. Eluting solvents—light petroleum, ether, $CHCl_3$ and ammoniacal $CHCl_3$ Ether-exhausted marc treated with EtOH (600 ml) and the evaporated extract boiled with acetone (100 ml), filtered and evaporated.

Cuscohygrine From ammoniacal $CHCl_3$ fraction Identified by co-chromatography (TLC, 2 systems, PC, 1 system), dipicrate m p and mixed m.p , IR, analysis (C and H).

ψ-Tropine. From ethanol-acetone extractions. Identified by co-chromatography (TLC, 2 systems, PC, 1 system), tigloyl ester,[3] purified by column chromatography at pH 6·8 and characterised by TLC (3 systems) and m p of picrate

Tropine. In trace amount with ψ-tropine. Detected by TLC (2 systems) after formation of tigloyl ester.

Hyoscyamine. Possibly trace quantities in $CHCl_3$ eluate. Detected by TLC (2 systems) and faint Vitali-Morin + ve reaction.

Hygrine Trace amount in $CHCl_3$ eluate, TLC (2 systems)

Aerial parts Powder (20 g) exhausted and fractionated as roots. Weak alkaloid reactions obtained with no identifiable alkaloids by TLC (3 systems), negative Vitali-Morin reaction.

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[2] W E SCOTT, R M MA, P S SCHAFFER and T D FONTAINE, *J Am Pharm Assoc* **46**, 302 (1957)
[3] W C EVANS and M WELLENDORF, *J Chem Soc* 1406 (1959)

Key Word Index—*Salpichroa origanifolia*, Solanaceae, tropane alkaloids.