Ethyl acetate ext Pedalin (m p and mixed m p, acid hydrolysis to yield pedalitin and glucose, R_f and co-chromatography with authentic samples).

Aqueous mother-liquor Added equal volume of 14% H_2SO_4, kept in a boiling water bath for 2 hr, cooled and extracted with ether and EtOAc EtOAc concentrate on dilution with acetone yielded a yellow solid, m p 185°, found to be a mixture of two glycosides (PC, R_f 0·45 and 0 60, H_2O) The pigments were separated by column chromatography on cellulose.

Dinatin-7-glucuronide. (R_f 0·45, eluted with water-saturated EtOAc containing 5–25% MeOH), decomposing at 221–223°, λ_{max} MeOH 270, 337 nm (no shift of Band II with NaOAc), hydrolysis with 10% H_2SO_4 in HOAc medium for 5 hr yielded dinatin and glucuronic acid

Diosmetin 7 glucuronide. (R_f 0·60, eluted with MeOH), decomposing at 210–212°, λ_{max} 268, 340 nm (no shift of Band II with NaOAc), hydrolysis as above yielded diosmetin and glucuronic acid

Comment. This is the first record of isolation of a dinatin glycoside and diosmetin glucuronide. Considerable difficulty was experienced in separating the glucuronides of the two isomers by fractional crystallization The occurrence of dinatin and pedalitin in the Pedaliacea is significant from the point of view of chemotaxonomy in view of the frequent records of 6-hydroxy or 6-methoxyflavones in families of the Tubiflorae [2,3] Dinatin glucuronide was also detected in the leaves of *Sesamum indicum* (Pedaliaceae) in addition to pedalitin and pedalin recorded earlier.[2]

[3] J B HARBORNE and C A WILLIAMS, *Phytochem* **10,** 367 (1971)

Key Word Index—Pedalium murex, Pedaliaceae, flavonoids, pedalitin, dinatin; diosmetin.

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SAPOTACEAE

CONSTITUENTS OF *MADHUCA LONGIFOLIA* LEAVES

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Plant. Madhuca longifolia syn. *Bassia longifolia. Uses* Medicinal,[1] seed fat a commercial commodity,[2] flowers rich in sugar—for fermentation (country liquor) [3,4] For all practical purposes identified with *Madhuca indica.*[5] *Previous work. Madhuca latifolia.* Seed fat,[6] seed saponin,[7,8] blossoms,[3,4] bark [9]

[1] B MUKERJI, *Indian Pharmaceutical Codex*, Vol I, p 144, CSIR (India), New Delhi (1953)

[2] *Wealth of India*, Vol VI, p 210, CSIR (India), New Delhi (1962)

[3] G J FOWLER, G D E BERHAM, S N BHATE, K H HASSAN, H MEHDIHASSAN and N N INUGANTI, *J Indian Inst Sci* **3,** 81 (1920)

[4] T N R RAO, C T DWARKANATH and D S JOHAR, *Food Sci* (*Mysore*) **10,** 88 (1961)

[5] P VAN RAYAN, *Blumea*, **10,** 122 (1960)

[6] T P HILDITCH and M B ICCHAPORIA, *J Chem Soc Indian* **57,** 44T (1938)

[7] B J HEYWOOD, G A R KON and L WARE, *J Chem Soc* 1124 (1939)

[8] B J HEYWOOD and G A R KON, *J Chem Soc* 713 (1940)

[9] Y C. AWASTHI and C R MITRA, *Phytochem* **7,** 1432 (1968)

Leaves. EtOH extr. fractionated successively with *n*-hexane, ether and ethyl acetate.

Hexane extract Chromatography, neutral Al_2O_3 *β-D-glucoside* of *β-sitosterol,* m p , mixed m p , *acetate,* m.p , mixed m p. and superposable IR, hydrolysed to β-sitosterol and glucose with 5% H_2SO_4 (alc) *Stigmasterol,* m.p., mixed m.p , *acetate,* m p , mixed m p , superposable IR and co-TLC *n-Hexacosanol,* m p , mixed m p , *acetate,* m p , mixed m p and IR.

New triterpene esters. Chromatographic fractions (benzene–hexane, 1 4) yielded an L-B and Noller's positive compound, m p. 152°, $C_{40}H_{68}O_3$ (Found C, 80·22, H, 11·52 Required C, 80·53, H, 11·40%), ν_{max} 3448 (free OH), 1709 (ester carbonyl) and 820 (trisubstituted double bond) cm^{-1} The ester on hydrolysis with 5% alcoholic KOH yielded *erythrodiol,* $C_{30}H_{50}O_2$, m p , mixed m.p , *acetate,* m p , mixed m p , superposable IR and co-TLC, and a fatty acid identified as *capric acid,* $C_{10}H_{20}O_2$, mol wt 172 (M^+), neutr equiv 170 Mass and NMR data of the ester favoured the attachment of the capric acid moiety at 3β —OH of erythrodiol and subsequently the structure of the new triterpene ester was assigned as 3β-caproxy-olea-12-en-28-ol In the mass spectra, the molecular ion peak was obtained at *m/e* 596 and a loss of 172 mass units ($C_{10}H_{20}O_2$) was recorded in the appearance of a peak at *m/e* 424, which on subsequent loss of 31 mass units (—CH_2OH) gave a prominent peak at *m/e* 393 The characteristic *retro*-Diels-Alder fragmentation pattern was observed with a peak at *m/e* 234 arising due to 'right half' of Δ^{12}-oleananes [10] Loss of 31 mass units (*m/e* 203, base peak) was also observed from this fragment which further substantiated the presence of free —CH_2OH at C-28 Other prominent peaks were at *m/e* 189, due to 'left half' of Δ^{12}-oleananes[11] and at *m/e* 133, due to further fragmentation of *m/e* 203 fragment in ring-E [10]

The NMR spectra of the ester further confirmed the presence of free —CH_2OH at C-28 as an AB type quartet (2H) centred around τ 6 65 ($J = 11$ c/s) appeared due to methylene protons of free primary hydroxyl group,[12] presence of α-proton at C-3 (1H) of 3β-acyloxy oleananes was observed as a triplet centred at τ 5 4 ($J = 8$ c/s)[12] and olefinic proton of Δ^{12}-oleananes was observed as an unresolved multiplet centred at τ 4 7 (1H)

Oleanolic acid palmitate The chromatographic fractions ($CHCl_3$–MeOH, 3 1) yielded another L-B and Noller's positive ester, m.p 145°, $C_{46}H_{78}O_4$, mol. wt 694 (M^+), ν_{max} 1739, 1709 (ester carbonyl and carboxyl) showed prominent peaks in the mass spectra at *m/e* 438 ($M^+ - 256$), *m/e* 248 (right half *retro*-Diels-Alder fragment), *m/e* 203 (248–COOH) and NMR peaks at τ 4 7 and τ 5 45 (see erythrodiol caprate *vide supra*) On hydrolysis with 5% alcoholic KOH, the ester gave *palmitic acid,* m p , mol wt 256 (M^+) and *oleanolic acid,* m p , mixed m p of acid and its methyl ester, IR and co-TLC. Oleanolic acid palmitate in crude form has earlier been reported from *Madhuca butyracea.*[14]

Ether fraction Traces of xanthophyll, m p 186°, λ^{cal}_{max} 424, 446, 472 nm, IR 3390 cm^{-1} (free OH). The mass spectra of the compound could not be recorded due to its decomposition *Flavonoid* m p > 325°, $C_{15}H_{10}O_8$, mol wt 318 (M^+), λ^{cal}_{max} 254, 378, with anhydrous aluminium chloride, λ^{alc}_{max} 266, 435 nm, penta-acetate, ($M^+ = 528$), m p 191°, hexamethyl ether, ($M^+ = 404$), m.p 155° Though colour reactions (Shinoda[15] and alkali) and UV

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[10] C R NOLLER, R A SMITH, C H HARRIS and J W WALKER, *J Am Chem Soc* **64,** 3047 (1942)

[11] H BUDZIKEWICH, J M WILSON and C DJERASSI, *J Am Chem Soc* **85,** 3688 (1963)

[12] J B THOMPSON, *Tetrahedron* **22,** 351 (1966)

[13] G N PANDEY and C R MITRA, *Tetrahedron Letters* **15,** 1352 (1967)

[14] Y C AWASTHI and C R MITRA, *Phytochem* **7,** 637 (1968)

[15] J SHINODA, *J Pharm Soc Japan* **48,** 214 (1928)

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.

[16] T A Geissman, in *Modern Methods of Plant Analysis* (edited by K Peach and M V Tracey), Vol III, p 464, Springer, Berlin (1955)

[17] L Jurd and R M Horowitz, *J Org Chem* **22**, 1618 (1957)

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SOLANACEAE

BOMBIPRENONE FROM *NICOTIANA TABACUM*

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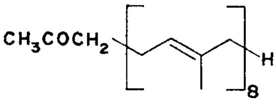
Abstract—Bombiprenone (6,10,14,18,22,26,30,34-octamethyl-5,9,13,17,21,25,29,33-pentatriacontaoctaen-2-one) has been isolated from flue-cured tobacco (*Nicotiana tabacum*) in yields of 0 1–0 6% dry wt. Plastoquinone-A was converted to bombiprenone by aerobic photo-oxidation, most probably via a hydroperoxide

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)

[2] M Toyoda, H Fukawa and T Shimizu, *Tetrahedron Letters* 3837 (1968)