tetrahydroxyxanthone, considered to be probably an artifact since it can be obtained by UV irradiation of maclurin [4].

Heartwood, upon cutting, showed pockets of pure, crystalline 1,3,6,7-tetrahydroxyxanthone which was collected with a knife and identified by direct comparison with authentic material. The absence of maclurin and other impurities in the sample was verified by mp, TLC and spectral means. The insolubility of the cmpd. precluded its presence in the C_6H_6 extract (20 g *ex* 6·0 kg), which was chromatographed on silica. Elution with solvent of gradually increasing polarity gave aliphatic ester (washed with petrol, mp 94–97°), 6-prenylpinocembrin (recryst. EtOH, 100 mg) and fatty acid (10 mg). The C_6H_6 softwood extract (15 g ex 3·0 kg) gave sitosterol and fatty acid. 6-Prenylpinocembrin was identified by direct comparison with a natural product from *Derris rariflora* (Mart.) Macbr. [5] and a synthetic one produced by prenylation (with 2-methyl-3-buten-2-ol, $BF_3.Et_2$ [6]) of pinocembrin. Alkylation of 5,7-dihydroxyflavanones is known to occur preferentially at C-6 [7].

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TRITERPENOIDS OF *CALLISTEMON LANCEOLATUS* LEAVES

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Key Word Index—*Callistemon lanceolatus*; Myrtaceae; triterpenoids; 2-α-hydroxyursolic acid.

Plant. Callistemon lanceolatus L. leaves (collected from Delhi University Campus).

Previous work. Ellagitannins [1], ellagic acid, 3,3′-di-*O*-methyl ellagic acid and 3,3′,4-tri-*O*-methyl ellagic acid from bark [2], esters of glucose with gallic and ellagic acids from seeds [2], anthocyanins [3] and betulinic acid [4] from flowers.

Present work. Air dried and powdered leaves exhaustively extracted with hot petrol (60–80°), Me_2CO and EtOH.

Petrol extract. The neutral portion of the petrol extract was chromatographed over Si gel with C_6H_6–EtOAc combination giving following compounds in the order—*Sitosterol*, identified by comparison, IR, mp and mmp 136–138°, $[\alpha]_D$ −36° with authentic sample and by conversion to acetate mp 126°, $[\alpha]_D$ −38°; *Erythrodiol*, mp 228–229°, $[\alpha]_D$ +74·6° (*c*, 0·98 $CHCl_3$), (positive LB and TNM tests), diacetate mp 184°; *Betulin*, mp 253–255°, $[\alpha]_D$ +19·2 (*c*, 0·78, $CHCl_3$) (positive LB test), diacetate mp 216–218°, $[\alpha]_D$ +20·5° (*c*, 2·1, $CHCl_3$), identities confirmed by direct comparison with authentic specimens in both cases. *Acetone extract*, on alkali extraction (KOH 10%) formed an emulsion. This on neutralisation with dil. HCl and extraction with EtOAc afforded green solid which was chromatographed over Si gel. Elution with EtOAc–C_6H_6 (1:9) yielded betulinic acid, mp 309–311°, $[\alpha]_D$ +9° ($CHCl_3$) (Co-IR, Co-TLC, positive TNM, L.B. and Noller's tests), methyl ester mp 221–223°, $[\alpha]_D$ +7·9, acetate mp 286–288°. Subsequent fractions yielded ursolic acid mp 287–288°, $[\alpha]_D$ +66·3° (MeOH) (positive L.B. and TNM test, Co-IR & Co-TLC), methyl ester mp 170–172°, $[\alpha]_D$ +61·2 ($CHCl_3$), acetate mp 246–47°. EtOAc–C_6H_6 (2:8) eluate gave a mixture of two unidentified compounds (A and B) which were finally separated by chromatography over Si gel after diazomethane methylation. Substance A, mp 126–130°; Substance B, mp 211–212° (positive LB and TNM tests). Final elution with EtOAc–C_6H_6 (2·5:7·5) afforded 2-α-hydroxyursolic acid, mp 243–44° R_f, 0·60 (MeOH–$CHCl_3$) (1:9), diacetate mp 197°, methyl ester mp 207–208°, $[\alpha]_D$ +48 (1·1, $CHCl_3$), methyl ester acetate mp 143–145°. MS of the methyl ester showed M^+ 486, 262 (DE ring fragment through RDA fission), 223 (AB ring fragment RDA), 203 (262-COOMe). NMR of methyl ester diacetate in CCl_4 showed δ 1·94 and 2·02 (OCOMe), 3·60 (COOMe) and a doublet at 4·68 (J 10 Hz) (C_3-H) indicating trans diaxial protons at C_2 and C_3. Confirmed by direct comparison (TLC, IR, NMR and MS). This is the second report of the occurrence of 2-α-hydroxyursolic acid in Myrtaceae; the first [5] described its co-occurrence with maslinic acid in *Psidium guaijava* leaves. The presence of compounds belonging to three related skeletons together in *Callistemon* is noteworthy.

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3-ETHYL-7-HYDROXYPHTHALIDE FROM *FORSYTHIA JAPONICA*

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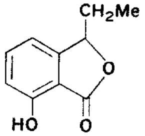
Key Word Index—*Forsythia japonica*; Oleaceae; essential oil; 3-ethyl-7-hydroxyphthalide.

Plant. *Forsythia japonica* Makino, stem bark. *Source.* Collected from the outskirts of Osaka-Fu, Japan. *Uses.* Medicinal. *Previous work.* Leaves of *F. coreana* Nakai and *F. suspensa* Vahl [1]. Bark and leaves of several *Forsythia* species [2]. *Present work.* In continuation of our investigations on the essential oil of *F. japonica*, we now report the occurrence of 3-ethyl-7-hydroxyphthalide (**1**).



(1)

The essential oil of the stem bark of *F. japonica* deposited a crystalline constituent, $C_{10}H_{10}O_3$, mp 78°, $[\alpha]_D^{25}$ +1·87 (1·01% in EtOH). UV λ_{max}^{EtOH} 235, 300 nm (log ϵ 2·34, 1·90) almost superimpossible with that of synthetic 3-ethyl-7-hydroxyphthalide [3]. NMR: $\delta_{ppm}^{CCl_4}$ (60 MHz, i.s. TMS) 1·03 (3H, *t*, –CH_2–Me), 1·89 (2H, *m*, –$\underline{C}\underline{H}_2$–Me), 5·35 (1H, *t*, –CH–O–CO–), 6·82 (2H, *d*, aromatic H), 7·44 (1H, *t*, aromatic H), 7·79 (1H, brod *s*, –OH). IR: ν_{max}^{KBr} 3500, 3020, 1740, 1605, 1478, 1195 cm^{-1}. MS: *m/e* (abundance %) 178 (37·8), 149 (100·0), 121 (33·5), 93 (11·7), 65 (16·5).

The acetate (C_6H_5N–Ac_2O) was purified by Al_2O_3 column chromatography. NMR: $\delta_{ppm}^{CCl_4}$ 0·99 (3H, *t*, –CH_2–Me), 1·88 (2H, *m*, –$\underline{C}\underline{H}_2$–Me), 2·34 (3H, *s*, –O–CO–Me), 5·24 (1H, *t*, –CH–O–CO–), 7·08 (2H, *t*, aromatic H), 7·55 (1H, *t*, aromatic H). IR: ν_{max}^{NaCl} 1768, 1370, 1189 cm^{-1}. Methylation with CH_2N_2 gave the ether. NMR: $\delta_{ppm}^{CCl_4}$ 0·99 (3H, *t*, –CH_2–Me), 1·88 (2H, *m*, –$\underline{C}\underline{H}_2$–Me), 3·95 (3H, *s*, ϕ–O–Me), 5·22 (1H, *t*, –CH–O–CO–), 6·86 (2H, *d*, aromatic H), 7·52 (1H, *t*, aromatic H). IR: ν_{max}^{NaCl} 1288, 1040 cm^{-1}. MS: *m/e* 192 (19·5), 175 (5·0), 162 (19·5), 163 (100·0), 146 (29·0), 135 (24·3), 105 (11·5), 77 (20·5). The compound was thus shown to be 3-ethyl-7-hydroxyphthalide (**1**).

This is its first isolation from a plant source and is significant from the biogenetic point of view since all phthalides, so far isolated from plants, have the same skeleton or a modification thereof.