$C_{34}H_{54}O_4$ requires C, 77.5; H, 10.3%); ν_{max}^{KBr} cm^{-1}: 885, 1250 and 1750. NMR (CCl_4): δ 0.78–1.15 (18H, 6 ter. Me). 1.65 (*s*, 3H, =C–C$\underline{H}_3$), 1.88 and 1.98 (*s*, 3H each, 2 OCOC$\underline{H}_3$), 4.35–4.70 (4H, *m*, =C$\underline{H}_2$, C–2H and C–3H).

Lupane-2α,3β-diol (**2**). The diol (**1**, 50 mg) in EtOAc (8 ml) was hydrogenated over PtO_2 for 6 hr. The dihydrodiol (**2**, 50 mg), mp 215°; $[\alpha]_D$ −20.0° (*c*, 0.3, $CHCl_3$) (Found: C, 80.8; H, 12.2. $C_{30}H_{52}O_2$ requires C, 81.0; H, 11.8%). ν_{max}^{KBr} cm^{-1}: 3550. NMR ($CDCl_3$): δ 0.86–1.08 (24H, 8 C-Me), 2.30 (2H, *s*, 2 × O$\underline{H}$), 3.00 (1H, *d*, *J* 10.5 Hz, 3-H) and 3.60 (1H, *m*, *W*1/2–23.0 Hz, 2-H). The acetonide [1] (**4**), mp 228°; $[\alpha]_D$ −22.0° (*c*, 0.3 $CHCl_3$) (Found: C, 81.3; H, 11.9. $C_{33}H_{56}O_2$ requires C, 81.7; H, 11.6%). ν_{max}^{KBr} cm^{-1}: 855, 1058, 111, 1165 and 1260. The diosphenol (**5**) [1] gave a positive ferric reaction; λ_{max}^{EtOH} nm: 273 (ε 7600); $\lambda_{max}^{EtOH-KOH}$ nm: 312 (ε 5800); $\lambda_{max}^{EtOH+HCl}$ nm: 273 (ε 7600).

2α-Acetoxy-lup-20(29)-en-3-one (**7**). The diol (**1**, 100 mg) was treated with Ac_2O–Py at 0° for 1 hr, the product worked up and chromatographed over $AgNO_3$–SiO_2. $CHCl_3$ eluates yielded lup-20(29)-en-2α,3β-diol 2-acetate (**6**, 60 mg), mp 270°, $[\alpha]_D$ −38.0° (*c*, 0.3 $CHCl_3$). ν_{max}^{KBr} cm^{-1}: 880, 1250, 1740 and 3550. NMR ($CDCl_3$); δ 0.77–1.10 (18H, 6 ter. methyls), 1.65 (3H, *s*, =C–Me), 2.05 (3H, *s*, –OCOC$\underline{H}_3$) 3.12 (1H, *d*, *J* 10.5 Hz, 3-H), 4.50–5.00 (3H, 2-H and =C$\underline{H}_2$). It was treated with excess of Jones' reagent. The product (**7**), mp 255°; $[\alpha]_D$ + 43.3° (*c*, 0.5 $CHCl_3$) was identical with 2α-acetoxy-lup-20(29)-en-3-one [3] (co-TLC, mmp and superimposable (IR).

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NEW PHENOLIC CONSTITUENTS OF *GREVILLEA ROBUSTA* WOOD

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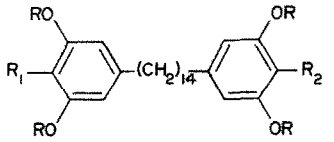
Key Word Index—*Grevillea robusta*; Proteaceae; grevillol; mono-norstriatol; bis-norstriatol.

Previous work has shown the presence of 5-*n*-tridecyl, 5-*n*-pentadecyl, 5-pentadeca-8-enyl and 5-pentadec-10-enyl resorcinols in the wood [1] and of rutin, 2,5-dihydroxycinnamic acid, methyl 4-hydroxy cinnamate and robustol and three minor related macrocyclic phenols in leaves [2] A thorough re-investigation of *Grevillea robusta* wood has now revealed the presence of three new phenolic components. Two of them, mono-norstriatol and bis-norstriatol, have been assigned structures as 1-(3,5-dihydroxyphenyl), 14-(3,5-dihydroxy 4-methylphenyl)-tetradecane (**1a**) and 1,14-bis-(3,5-dihydroxyphenyl) tetradecane (**1b**) respectively based on spectral data. The UV and IR spectra showed them to be phenolic in nature and PMR and mass spectral comparison with striatol (**1c**) [3] indicated them to lack one and two *C*-methyl groups respectively. Although the methyl ether of the latter is known as a synthetic product [3], this is the first report of its natural occurrence; the former is an entirely new natural product.



(**1a**) R = R_2 = H; R_1 = Me
(**1b**) R = R_1 = R_2 = H
(**1c**) R = H; R_1 = R_2 = Me
(**1d**) R = COMe; R_1 = Me; R_2 = H
(**1e**) R = R_1 = Me; R_2 = H
(**1f**) R = COMe; R_1 = R_2 = H
(**1g**) R = Me; R_1 = R_2 = H

The occurrence of compounds with the diphenyltetradecane skeleton in *G. robusta* is of interest, the only member of this class till now being striatol from the wood of *G. striata*. The two compounds are also of biogenetic interest, mono-norstriatol being a possible intermediate in the elaboration of striatol [4].

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ unless stated otherwise using TMSi as an internal standard and MS were recorded by direct inlet method at 70 eV ionization potential.

Isolation. Air dried and powdered material (2.3 kg) (collected in Dehli University Campus) was extracted exhaustively with C_6H_6, Me_2CO and EtOH respectively.

Benzene extract. On concentration and keeping in the refrigerator this deposited a solid which when subjected to repeated dissolution in ether and precipitation by light petroleum afforded a brown solid, crystallized as colourless needles (16 g), mp 79–80°, negative ferric colour, positive test for resorcinol derivatives with $Hg(NO_3)_2$, identified as grevillol [1].

Acetone extract. This was evaporated to dryness *in vacuo*; 20 g of reddish syrup was chromatographed over Si gel affording besides grevillol, three more compounds.

Mono-norstriatol (**1a**). From C_6H_6–EtOAc (9:1) fractions, brownish syrupy liquid (2.2 g). (Found: C, 75.9; H, 9.6. $C_{27}H_{40}O_4$ requires C, 75.7; H, 9.3%.) λ_{max}^{MeOH} 273, 276 nm; +KOH 281, 283 nm. ν_{max}^{KBr} 3500 br (OH), 2976, 1621, 1595, 1440, 1144, 1068, 830, 719 and 693 cm^{-1}; MS: *m/e* 428 (M^+) *tetraacetate* (**1d**) with Py–Ac_2O at room temp., colourless syrup, PMR δ 6.80 (*br*, 5 H, Ar-H), 2.58 (*t*, 4 H, Ar-CH_2), 2.24 (*s*, 6 H, phenolic O*Ac*), 2.19 (*s*, 6 H, phenolic O*Ac*), 1.92 (*s*, 3 H, Ar-Me), 1.25 (*br s*, 24 H, $-(CH_2)_{12}-$); *tetramethyl ether* (**1e**) with K_2CO_3–$(Me)_2CO$–$(Me)_2SO_4$, brown syrup. PMR: δ 6.53 (*br*, 5 H, Ar-H), 4.06 (*s*, 6 H, –OMe), 4.01 (*s*, 6 H, –OMe), 2.80 (*t*, 4 H, Ar-CH_2), 2.28 (*s*, 3 H, Ar-Me), 1.47 (*br s*, 24 H, $-(CH_2)_{12}-$).

Bis-norstriatol (**1b**). From C_6H_6–EtOAc (17:3) eluates, brownish syrup, crystallized as colourless needles (C_6H_6) (5.3 g) mp 97–99°. (Found: C, 75.1; H, 8.9. $C_{26}H_{38}O_4$ requires C, 75.3; H, 9.1%.) λ_{max}^{MeOH} 276 nm; +KOH 282 nm. ν_{max}^{KBr} 3390 (OH), 2950, 1623, 1595, 1480, 1156, 998, 831, 727 and 676 cm^{-1}. PMR(DMSO-D_6, δ) 9.8 (*s*, 4 H, Ar-OH), 6.18 (*br*, 6 H, Ar-H), 2.4 (*t*, 4 H, Ar-CH_2), 1.23 (*br. s*, 24 H $(CH_2)_{12}$–). MS: *m/e* 414 (M^+) 167, 163, 149, 137, 124 (base), 123, 71, 57 and 43. *Tetraacetate* (**1f**) by Py–Ac_2O method in cold, colourless syrup, PMR 6.75 (*br*, 6 H, Ar-H), 2.52 (*t*, 4 H, Ar-CH_2), 2.1 (*s*, 12 H, phenolic O*Ac*), 1.18 (*br s*, 24 H, $-(CH_2)_{12}-$), *tetramethyl ether* (**1g**) by K_2CO_3–$(Me)_2CO$–$(Me)_2SO_4$ method. Colourless rods (EtOAc), mp 63–64°, PMR: δ 6.39 (*br*, 6 H, Ar-H), 3.75 (*s*, 12 H, –OMe), 2.55 (*t*, 4 H, Ar-CH_2), 1.28 (*br*, 24 H, $-CH_2)_{12}-$). MS: *m/e* 470 (M^+) 165, 152, 151, confirmed by direct comparison with synthetic sample [3] (co-TLC, mmp, co-IR).

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TWO NEW COUMARINS FROM *TODDALIA ACULEATA**

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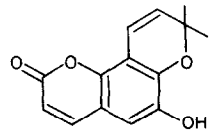
Key Word Index—*Toddalia aculeata*; Rutaceae; alkaloids; coumarins; norbraylin; 5,7,8-trimethoxycoumarin.

Toddalia aculeata was collected and supplied by Mukerjee & Co., Algarah, Darjeeling, India and is widely distributed in subtropical Himalayas, Southern India and Ceylon. The plant is used in medicine as a tonic, stimulant, and antipyretic.

The plant has been extensively investigated and a number of coumarins and alkaloids have been reported [1,2]. From the chloroform extract of the stem two new coumarins, norbraylin (**1**) and 5,7,8-trimethoxycoumarin have been isolated. In addition 3 alkaloids, robustine, dictamnine and γ-fagarine, and 2 coumarins, bergapten and luvangetin, have been isolated for the first time from this plant.



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The total chloroform extract of the stem was chromatographed over silica gel column and eluted successively with C_6H_6, C_6H_6–$CHCl_3$, $CHCl_3$ and finally $CHCl_3$–MeOH. Some of the fractions were rechromatographed for further purification. From the first few fractions toddalinine, robustine, skimmianine, dictamnine, bergapten, luvangetin and isopimpinellin have been isolated. The final fractions were further separated into phenolic and neutral compounds. The phenolic portion was purified by passing through a short column of Si gel using hexane–Me_2CO (4:1). One compound crystallized as needles, mp 132–34°, M^+ 244 (Found: C, 69.0; H, 5.0. $C_{14}H_{12}O_4$ requires C, 68.9; H, 4.9%). IR, ν_{max} (cm^{-1}) 1720 (C=O of α-pyrone) and 3535 (phenolic OH). NMR ($CDCl_3$, τ60 MHz,) 3.13 and 4.3 (two, *d*, J = 10 Hz) vinylic H, 8.5 (s, *C*–Me_2) presence of 2,2-dimethylchromene ring; 3.7 and 2.5 (two *d* J = 10 Hz) 3- and 4-H of coumarin ring and 3.14 (*s*, 5-H). Hence the compound should have structure (**1**). The linear structure was ruled out as its TLC and mmp was not identical with norluvangetin, MS (*m/e*): 244 (28%), 229 (100) M-15; 243 (2) M-1; 201 (9) (M-43). The coumarin was methylated with diazomethane which gave a crystalline monomethyl ether, mp 150° (lit. [3] mp 150°). The MS fragmentation was consistent with braylin. Thus this phenolic compound is norbraylin, not reported previously. The neutral fraction was purified by passing through a short column of alumina

* NCL communication No. 1969.