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SHORT REPORTS

A NEW TRITERPENE FROM *PTEROCARPUS SANTALINUS* BARK

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Key Word Index—*Pterocarpus santalinus*; leguminosae; triterpenes; betulin; lup-20(29)-en-2α,3β-diol.

Past work. On heartwood [1], sapwood [2], bark [3] and leaves [4].

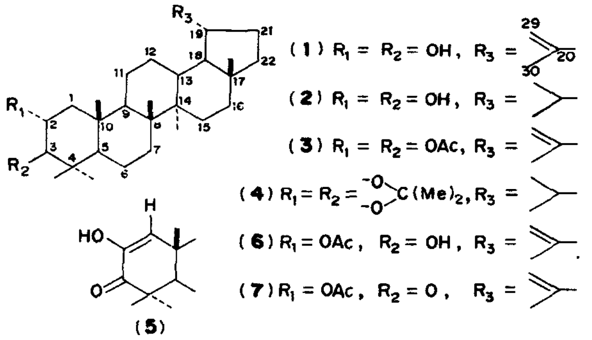
Present work. Six triterpenes isolated previously [3] from the bark of *Pterocarpus santalinus* included a new compound 2α-hydroxy-epilupeol. Reinvestigation of the bark has now produced betulin and another new lupene diol whose structure is described here.

The new triterpene, mp 234°, $C_{30}H_{50}O_2$ (M^+ 442) showed the presence of hydroxyl(s) (3530 cm^{-1}) and exo =CH_2 (885 cm^{-1}) groups in its IR spectrum. The NMR spectrum had signals for six tertiary methyl groups (δ 0.85–1.10), a vinylic methyl (δ 1.66), two hydroxylic protons (δ 2.30, lost on equilibration with D_2O), two carbinol methine protons at δ 3.00 (*d*, *J* 10.5 Hz) and 3.60 (*m*, *W*1/2 = 23.0 Hz) and exo = CH_2 protons at δ 4.62 and 4.72 (*d* each, *J* 1.8 Hz). Catalytic hydrogenation of the diol (**1**) yielded a dihydro-derivative (**2**), mp 215° which lacked vinylic methyl and exo=CH_2 signals in its NMR sepctrum. The diol (**1**) formed a diacetate (**3**), mp 130°. Its NMR spectrum had two acetoxyl signals and the two associated methine protons were shifted downfield.

These data suggested the compound to be a lupene diol and this was confirmed by the MS of the compound which had diagnostically important fragments (**a**), (**b**), (**c**) and (**d**) (Scheme 1) further showing the location of the two hydroxyl functions on rings A and/or B [3].

The dihydrodiol (**2**) was cleaved by periodate, formed an acetonide (**4**), mp 228° and a diosphenol (**5**) by Jones' oxidation, λ_{max} 273 nm. Evidently the two hydroxyls were placed vicinally. The multiplicity of the carbinol methine signal at δ 3.00 (*W*1/2 = 23.0 Hz) in the NMR spectrum of the diol (**1**) ruled out any hydroxylation in ring B [3]. In ring A the two hydroxyls were preferred at C-2 and C-3 for biogenetic reasons.

The diequatorial orientation of the two hydroxyls (2α,3β) was indicated by the diaxial coupling of the C-3 proton signal (*J* 10.5 Hz) and the large *W*1/2 value of the C-2 proton signal (23.0 Hz) [7]. Chemical proof for the α-orientation of C-2 hydroxyl was obtained by partial acetylation of the diol (**1**) which yielded the 2-acetoxy-3-hydroxy compound (**6**), mp 270°. On Jones' oxidation this yielded a 2-acetoxy-3-keto compound (**7**), mp 254° which was identical with 2α-acetoxy-lup-20(29)-en-3-one obtained from lup-20(29)-en-2α,3α-diol [3].

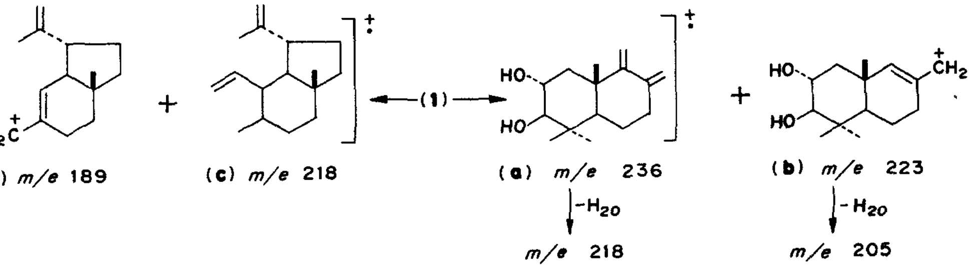


Scheme 1.

Thus the complete structure of the new triterpene diol was established as lup-20(29)-en-2α,3β-diol (**1**).

EXPERIMENTAL

Isolation. The $CHCl_3$ extract of the dried powdered bark (2 kg) was chromatographed on a Si gel column which yielded, in addition to the earlier reported compounds [3], betulin, mp 258° (co-TLC, mmp and superimposable IR with an authentic sample) and the new compound (**1**, 350 mg); crystallised as colourless needles, mp 233–34°; $[\alpha]_D$ + 12.5° (*c*, 0.2 $CHCl_3$), IR and NMR spectra given in the text. MS *m/e* (rel.int.): 442 (64), 427 (20), 424 (18), 332 (10), 236 (11), 223 (80), 218 (6), 203 (47), 189 (72) and 43 (100). The diacetate (**3**), mp 130°, $[\alpha]_D$ + 28.0° (*c*. 0.2 $CHCl_3$) (Found: C, 77.6; H, 10.3.



Scheme 2.

$C_{34}H_{54}O_4$ 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*, =CH_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 =CH_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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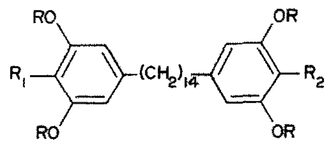
Key Word Index—*Grevillea robusta*; Proteaceae; grevillol; mono-norstriatol; bis-norstriatol.

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.



(**Ia**) R = R_2 = H ; R_1 = Me
(**Ib**) R = R_1 = R_2 = H
(**Ic**) R = H ; R_1 = R_2 = Me
(**Id**) R = COMe ; R_1 = Me ; R_2 = H
(**Ie**) R = R_1 = Me ; R_2 = H
(**If**) R = COMe; R_1 = R_2 = H
(**Ig**) 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].