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Phytochemistry, 1975, Vol. 14, pp. 1447–1448. Pergamon Press. Printed in England.

A NEW PENTACYCLIC TRITERPENE LACTONE FROM *DILLENIA INDICA**

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(*Received* 8 *August* 1974)

Key Word Index—*Dillenia indica*; Dilleniaceae; myricetin; sitosterol; betulinic acid; betulinaldehyde; betulin; lupeol; a new hydroxylactone—3β-hydroxy-lupane-13β, 28-lactone.

Plant. Dillenia indica Linn is an evergreen tree native to India. *Uses.* Its bark and leaves are astringent [1]. *Previous work.* On trunk bark [2], on leaves [3].

Present work. Air-dried powdered stem-bark was successively extracted with light petrol, $CHCl_3$ and MeOH. Light petrol extract was dried and separated into neutral and acidic fractions by the usual method. The neutral fraction on repeated chromatography on SiO_2 column afforded betulinaldehyde, m.p. 199–200° $[\alpha]_D^{26}$ + 28°,† betulin, m.p. 254–255° $[\alpha]_D^{27}$ + 22°, Lupeol, m.p. 211–212° $[\alpha]_D^{29}$ + 27°, sitosterol, m.p. 137° $[\alpha]_D^{28}$ − 36° and the acidic fraction yielded only betulinic acid, m.p. 305–306° $[\alpha]_D^{27}$ + 6·35°. These compounds were identified by comparison with authentic samples (m.m.p., co-TLC, superimposable IR). The isolation of betulinic acid, betulinaldehyde, betulin and lupeol showed a remarkable biogenetic sequence rarely encountered in a plant source. The $CHCl_3$ extract yielded only betulinic acid and betulin.

The dried MeOH extract was re-extracted with $CHCl_3$ to remove nonglycosides and the mixture of glycosides, which could not be separated on SiO_2, was hydrolysed with 5% methanolic HCl. The only sugar identified was D-glucose (PC). The aglycone fraction was separated into acidic and neutral parts. The acidic part yielded only betulinic acid, and the neutral part, on column chromatography on SiO_2, afforded sitosterol, betulin, hydroxylactone B of betulinic acid [4] along with the flavonol myricetin, m.p. 358–360°, acetate, m.p. 214–216° and identified by comparison with an authentic sample (m.m.p., Co-TLC, superimposable IR, UV). Hydroxylactone B was most probably an artefact formed by influence of acid on betulinic acid.

Besides this series of known compounds C_6H_6:$CHCl_3$ (4:1) eluate from the chromatogram yielded a triterpene (+ve Liebermann–Burchard test −ve, $C(NO_3)_4$) m.p. 325° (*d*), $[\alpha]_D^{27}$ + 63·4°. $C_{30}H_{48}O_3$ (Found: C, 78·45; H, 10·42%; Calc. for $C_{30}H_{48}O_3$, C, 78·89; H, 10·59%) MW 456 by MS. Acetate m.p. 319–320° $[\alpha]_D^{27}$ + 82·1°. IR, 1754 cm^{-1} (5-membered lactone) and 3350 cm^{-1} (hydroxyl), suggestive of a hydroxylactone. This lactone was different from hydroxylactone A and B by comparison with authentic samples [4].

On oxidation with Jone's reagent it gave a keto compound, m.p. 328–330° $[\alpha]_D^{27}$ + 70°; IR, 1689 and 1754 cm^{-1}. The ketone gave a positive Zimmerman's test and was reduced back to the original compound with $NaBH_4$ which proved the β conformation of OH group at C-3. Studies of its MS pattern [5] (prominent peak for M − 43 unit for *iso*propyl) NMR spectra [6] and also on biogenetic ground, indicated the compound to be in the lupane series. It was not identical with dihydrothurberogenin [7] or the dihydrolactone produced by mercuric acetate oxidation of acetyl betulinic acid [8].

The compound was reduced by $LiAlH_4$ to give a triol m.p. 280–281° $[\alpha]_D^{27}$ + 34°, (Found: C,

* Presented at Annual Convention of Chemists (India) December 23–30, 1973.

† Unless otherwise stated, all $[\alpha]_D$ values are in $CHCl_3$.

78·31; H, 11·35%. Calc. for $C_{30}H_{52}O_3$, C, 78·20; H, 11·38%). IR spectra showed no CO. Acetylation (at room temperature and at 130°) gave a diacetate (without any trace of triacetate) m.p. 230–231° $[\alpha]_D^{27}$ + 32° (found: C, 74·89; H, 10·42; acetyl, 15·59, calc. for $C_{34}H_{56}O_5$, C, 74·95; H, 10·36; acetyl, 15·72%). Stability of this diacetate towards CrO_3 proved that the OH-group must be tertiary one i.e. at C – 13. The triol diacetate was dehydrated with BF_3 in dry benzene [9], purified on a $AgNO_3$ impregnated silica gel column, to give a major fraction which on crystallization ($CHCl_3$–MeOH) yielded a pure compound m.p. 295–296° $[\alpha]_D^{27}$ + 70·2°. Although the compound gave yellow colour with $C(NO_3)_4$, its IR spectra showed no absorption for a trisubstituted double bond. UV210 (ϵ = 5650) 215 (4520) and 220 nm (3650), were indicative of a tetrasubstituted double bond [10]. On oxidation with CrO_3 in HOAc [11] a conjugated ketone was obtained, m.p. 290° $[\alpha]_D^{27}$ + 65°. IR 1690 cm^{-1}, and UV, at 242 nm (ϵ = 13520) without any absorption for vinylic proton in NMR. Thus the position of double bond introduced by dehydration of triol-diacetate is most likely to be at C 13(18). In view of the evidence outlined above the structure of the new hydroxylactone is suggested to be 3β-hydroxy-lupane-13β-28-lactone (**1**).

Acknowledgement—The authors thank Dr U. R. Ghatak, Indian Association for the Cultivation of Science, Calcutta-32 for NMR spectra.

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Phytochemistry, 1975, Vol. 14, pp. 1448–1450. Pergamon Press. Printed in England.

ASEBOTIN AND ITS AGLUCONE FROM THREE SPECIES OF *RHODODENDRON*

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(*Received* 10 *July* 1974)

Key Word Index—*Rhododendron canescens*, *R. nudiflorum*, *R. roseum* and *R. calendulaceum*; Ericaceae; dihydrochalcones; asebotin; 2′,6′,4-trihydroxy-4-methoxydihydrochalcone.

In the course of a biochemical systematic investigation of *Rhododendron* (Ericaceae), we isolated two dihydrochalcones, one of which was not previously reported from Nature. In a recent review, Bohm [1] noted that there are only 13 naturally occurring dihydrochalcones including phloridzin (2′,4′,6′,4-tetrahydroxydihydrochalcone 2′-*O*-glucoside) and asebotin (the 4′-*O*-methyl ether of