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ULMACEAE

TRITERPENOID ALCOHOLS FROM *TREMA ORIENTALIS**

L. OGUNKOYA, O. O. OLUBAJO and D. S. SONDHA
Department of Chemistry, University of Ife, Ile-Ife, Nigeria

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Key Word Index—*Trema orientalis;* Ulmaceae; simiarenol; sitosterol.

The most polar fractions from the chromatographic fractionation of the neutral portion of the light petrol. extract of the stem-bark of *Trema orientalis* showed (TLC, IR) the presence of a number of alcohols with very close R_fs. Careful and repeated fractionation over alumina gave four colourless crystalline triterpenoid alcohols, the least polar of which was identified as simiarenol[1] (3-hydroxy-friedohop-5-ene, 0·003% based on air-dried material) and the most polar as β-sitosterol. The other two were not present in sufficient quantity for characterization.

The identity of simiarenol was deduced from the following data: M.p. 205–206°, $[\alpha]_D$ +47·7° (*c* 0·79 in $CHCl_3$) (lit. 209° + 50·8°). (Found: C, 84·07; H, 11·63. Calc. for $C_{30}H_{50}O$: C, 84·44; H, 11·81%.) IR: 3500 (OH), 810, 830, cm^{-1} (tri-substituted d.b.). NMR (60 MHz): 4·37 (1 vinyl H), 6·53 (3α —H) and sharp methyl signals from 8·85–9·23τ (8 methyls). Acetylation gave colourless crystalline acetate with the expected NMR and IR; m.p. 210° $[\alpha]_D$ +67·1° (*c* 0·64 in $CHCl_3$) (lit. 209°, +73·9°). (Found: C, 81·56; H, 11·19. Calc. for $C_{32}H_{52}O_2$: C, 81·99; H, 11·18%.) Oxidation with Jones reagent gave simiarenone, IR 1705 cm^{-1}; m.p. 209° $[\alpha]_D$ +19·4° (*c* 1·6 in $CHCl_3$) (lit. 207–208°, +20°). Simiarenone-DNP: 277–279° (lit. 275°). Reduction of the ketone with either LAH or $NaBH_4$ gave predominantly episimiarenol m.p. 195°, $[\alpha]_D$ +46·3° (*c* 0·58 in $CHCl_3$) (lit. 197–198, +46·8°) together with smaller quantities of simiarenol (TLC, m.m.p.). Episimiarenol also forms a crystalline acetate (IR, NMR) m.p. 188–189° $[\alpha]_D$ + 33° (*c* 0·51 in $CHCl_3$) (lit. 188–189°, +48°).

The key evidence in the identification of simiarenol was provided by MS of the alcohol and its ketone. The spectra gave M^+ *m/e* 426 ($C_{30}H_{50}O$) and 424 ($C_{30}H_{48}O$) respectively with strong peaks in both at *m/e* 274 (base), 259 (274-Me) and 231 (274-C_3H_7) consistent with the presence of 3-OH, 5(6) C=C and $(Me)_2CH$-functions. Simiarenol and its ketone are the only known pentacyclic triterpenes with these structural features in the molecule.

Sitosterol was identified by comparison (IR, NMR, TLC and m.m.p.) with an authentic sample. The yet unidentified alcohols have been shown to be isomeric pentacyclic triterpenoid compounds ($C_{30}H_{50}O$) with 3-OH and 9(11) C=C (MS).

EXPERIMENTAL

The neutral fraction, a dark gummy mass (35 g) obtained from the light petrol. extract of the air-dried powdered stem-bark (5 kg), was chromatographed over alumina III. The less polar compounds, which consisted mainly of carboxy derivatives of long-chain hydrocarbons, were eluted with light petrol. and light

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* L. OGUNKOYA, O. O. OLUBAJO and D. S. SONDHA, *Phytochem.* **11**, 2361 (1972).

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petrol.–benzene 1:1. Further elution with Et_2O–MeOH 9:1 gave a crude mixture (12·5 g) of alcohols (TLC, IR) which was rechromatographed over alumina II. Careful elution with benzene (TLC controlled) gave simiarenol (150 mg) as pure colourless crystals. Further elution gave a mixture of the two unidentified alcohols followed finally by β-sitosterol.

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VERBENACEAE

LAMIIDE FROM *CHASCANUM CERNUUM**

H. RIMPLER
WE Pharmakognosie der Freien Universität Berlin, Berlin, Deutschland

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Plant. Chascanum cernuum (L.) E. MEY. *Source.* South Africa, Cape, District Simonstown.

Leaf and stem. (145 g). Isolation by standard procedures[1] gave an impure iridoid-fraction with one main constituent. Column chromatography on silica gel (*n*-BuOH–MeOH–H_2O, 4:1:5) followed by gel filtration on Sephadex afforded 1·7 g of a pure amorphous compound (1·2%). The properties of this compound and of its penta- and hexa-acetates are identical with those reported[2] for lamiide and its acetates respectively (NMR, UV, IR, optical rotation, m.p.). The MS is in agreement with this structure.

The penta-acetate is identical with an authentic sample, which was kindly provided by Dr. M. L. Scarpati, University of Rome.

Voucher specimens are deposited in WE Pharmakognosie der Freien Universität Berlin.

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* Part IV in the series "Iridoids and Ecdysones from Verbenaceae". For Part III see *Phytochem.* **11,** 3096 (1972).

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