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CHEMICAL CONSTITUENTS OF *SCHEFFLERA SP.*

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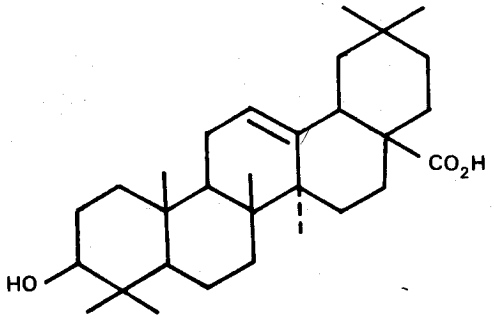
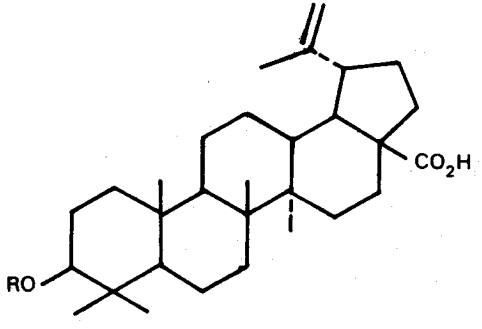
Abstract

Oleanolic acid (1), betulinic acid (2), D-glucose, D-xylose and L-rhamnose have been identified from the hydrolyzed aqueous ethanol extract of the leaves of Schefflera sp. (Araliaceae).

Schefflera sp. (local name: Hanumarn-prasarnguy) is an ornamental plant which usually grows up to 2-3 m tall. Its leaves are used in Thai folk remedies for relieving asthmatic attack. Recent pharmacological results indicated that the aqueous extract of the leaves relaxed smooth muscle of the isolated guinea-pig tracheal chain.[1-2]



(1)



(2), R = H

(3), R = $-\overset{O}{\overset{\|}{C}}CH_3$

The acid hydrolysis of the 95% ethanol extract of the dry leaves gave sapogenins which were purified by column chromatography on silica gel to give oleanolic acid (1) and betulinic acid (2). The paper chromatographic examination of the aqueous hydrolysate revealed the presence of D-glucose, D-xylose and L-rhamnose.

A voucher specimen (no. BKF73996) of the plant material has been deposited at the Herbarium, Forest Department, Ministry of Agriculture, Bangkok, Thailand.

Analyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were recorded on either a Varian EM360L or A60D instrument at 60 MHz. The mass spectra were measured with a Dupont 490F GC-MS instrument by direct inlet.

The dried powdered leaves (300.0 g) were extracted with 95% ethanol in a Soxhlet apparatus; the extract was filtered and evaporated to give a dark brown residue (95.8 g). Hydrolysis of this crude product with 4N aq. HCl for 4 h gave a brown precipipate which was collected and dried *in vacuo*. This product (25.5 g) was chromatographed on a column of silica gel (1.3 kg). Successive fractions obtained by gradient elution with hexane-ether were combined on the basis of their behavior on t.l.c., and evaporated to give a mixture of oleanolic acid (1) and betulinic acid (2) as a colourless powder (9.4 g). The mixture (0.7 g) was further purified by preparative layer chromatography using hexane-ether (1:1) as the developing solvent. The chromatograms were sprayed with water whereupon two bands appeared. The upper band gave betulinic acid (0.3 g) and the lower band yielded oleanolic acid (0.3 g).

Oleanolic acid (1): Compound (1) crystallized from 95% ethanol as needles, m.p. 303-307° (lit[3] 310°) (Found: C, 79.0; H, 10.3. Calc. for $C_{30}H_{48}O_3$: C, 78.9; H, 10.6%). ν_{max} (KBr) 3600-3000 (broad), 1675, 1655, 1025, 990 cm^{-1}. N.m.r. ($CDCl_3$): δ 1.20-2.00 (m, 23H, $-CH_2-$ and -CH-); 0.62-1.22 (7 × CH_3); 4.25 (m, 1H, -CH-0); 5.22 (m, 1H, -C = CH). Mass spectrum: m/e 456 (3%), 248 (64), 207 (15), 203 (35), 133 (14), 95 (27), 83 (36), 69 (60), 57 (84), 43 (100).

Betulinic acid (2): Compound (2) crystallized from methanol as needles, m.p. 268-275° (lit[4] 275-278°) (Found: C, 78.5; H, 10.5. Calc. for $C_{30}H_{48}O_3$: C, 78.9; H, 10.6%). The melting point was undepressed on admixture with an authentic sample. The infrared spectra (KBr) of the two samples were also identical. ν_{max} (KBr) 3660-3300 (broad), 1695, 1460, 1380 cm^{-1}. N.m.r. ($CDCl_3$) δ 0.77-0.93 (5 × CH_3); 1.27-2.60 (m, 25H, $-CH_2-$and-CH-); 1.68 (m, 3H, $CH_3-C=C$); 3.03 (m, 1H, -C=C-CH-); 3.17 (m, 1H, -CH-O); 4.61 (m, 1H, -C=CH); 4.75 (m, 1H, -C=CH). N.m.r. ($CDCl_3$, 400 MHz) 0.78, 0.82, 0.93, 0.96, 0.98, 1.68 (6 × CH_3), 3.17 (dd, J = 5, 11.2 Hz, 1H, -CH-0); 4.61 (dd, J = 1.4, 2.0 Hz); 4.75 (d, J = 2.0 Hz). Mass spectrum: m/e 456 (18%), 248 (18), 189 (59), 135 (22), 95 (46), 81 (51), 69 (63), 55 (74), 43 (100).

A mixture of compound (2) (0.13 g), acetic anhydride (6.0 ml) and pyridine (20 drops) was stirred under N_2 at room temperature for 20 h. Evaporation of the excess acetic anhydride gave a brown residue. A suspension of the residue in water (15.0 ml) was extracted with chloroform (3 × 15 ml) and the combined chloroform layer was then washed with 10% aq. H_2SO_4 (2 × 10 ml), water (3 × 10 ml), dried over anhydrous sodium sulfate and evaporated. The crude product was subjected to chromatography on a column of silica gel using hexane–ether (9:1) as the eluting solvent to give the expected acetyl derivative (3) as a powder (0.10 g) which crystallized from aqueous ethanol as needles, m.p. 283–285° (lit[4] 269–271°) (Found: C, 77.4; H, 10.1. Calc. for $C_{32}H_{50}O_4$: C, 77.1; H, 10.1%). ν_{max} (KBr) 3100–3560 (Broad), 1740, 1698, 1460, 1372, 1245 cm^{-1}. N.m.r. ($CDCl_3$): δ 0.9–1.07 (5 × CH_3); 1.32–2.67 (m, 25H, $-CH_2-$ and -CH-); 1.83 (m, 3H, C=C-CH_3); 2.20 (s, 3H, -C-CH_3); 3.20 (m, 1H, C=C-CH); 4.80 (m, 1H -C-O-CH); 4.93 (m, 1H, -C=CH); 5.07 (m, 1H, -C=CH). Mass spectrum: m/e 498 (4%), 452 (14), 438 (26), 395 (15), 248 (36), 203 (42), 189 (67), 135 (27), 95 (36), 55 (52), 43 (100).

Characterization of the sugar moieties: Paper chromatography of the above hydrolysate using phenol–H_2O (3:1) revealed the presence of D-glucose, D-xylose and L-rhamnose (R_f 0.39, 0.49 and 0.62, respectively). The spots visualized by spraying with aniline hydrogenphthalate were identical with those of the authentic sugars.

Acknowledgements

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References

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บทคัดย่อ

จากการสกัดและตรวจหาสูตรโครงสร้างของสารในใบของต้นหนุมานประสานกาย *(Schefflera sp.)* พบว่ามีสาร Oleanolic acid (1), Betulinic acid (2), D-Glucose, D-Xylose และ L-Rhamnose.