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S. K. Srivastava

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A NEW TRITERPENOID SAPONIN FROM *SCHEFFLERA IMPRESSA*

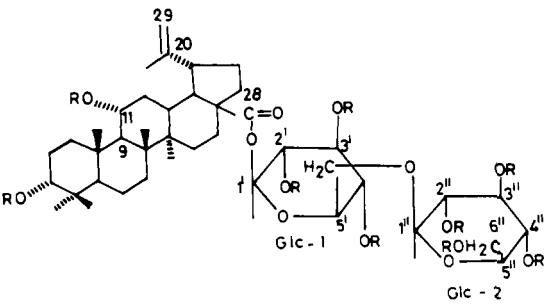
S.K. SRIVASTAVA

Central Institute of Medicinal and Aromatic Plants, Lucknow, India

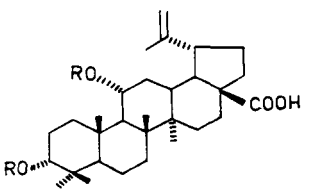
ABSTRACT.—A new triterpenoid saponin, 3α,11α-dihydroxylup-20(29)-en-28-oic acid 28-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside [**1**], has been isolated from the bark and stem of *Schefflera impressa*. Its structure has been deduced from spectroscopic data and by chemical correlation with compounds of established structure.

In previous reports (1–4) we described the isolation and identification of sixteen compounds, including four new triterpenoid saponins and sapogenins, from the stem and bark of *Schefflera impressa* C.B. Clarke (Araliaceae). The present communication describes the isolation and structure elucidation of a new triterpenoid saponin impressoside A, 3α,11α-dihydroxylup-20(29)-en-28-oic acid 28-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside [**1**] from the stem and bark of *S. impressa*. The co-occurrence of saponin **1** and free impressic acid [**2**] in *S. impressa* (4) is of chemotaxonomic importance due to their structural similarity with the main constituent and saponins of *Schefflera octophylla* (5–8), which is used in Chinese and Vietnamese folk medicine as an antipyretic, anti-inflammatory, analgesic, and tonic and as a drug for the treatment of liver disease.

The stem and bark of *S. impressa* were extracted with MeOH, and the crude saponin fraction on chromatographic separation afforded saponin **1**, mp 268–270°, $[\alpha]_D$ +0.36° (MeOH, $c = 0.1$). It gave a positive Feigl test for glycosides and a yellow color with Liebermann-Burchard reagent, suggesting that it may be a lupene glycoside (9). Compound **1** had distinctive absorptions in its ir spectrum due to hydroxyl (3420), ester (1746, 1066), and exocyclic



1 R=H
4 R=Ac



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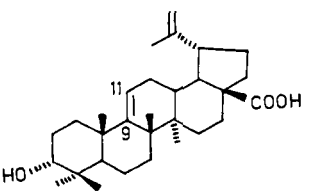

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methylene (1639 and 900 cm^{-1}) groups. It is to be noted that the last two bands are generally encountered with $\Delta^{20(29)}$-lupene derivatives (6,10).

The ^{1}H-nmr spectrum of **1** (Me_2CO-d_6) showed the presence of five tertiary methyls, two olefinic protons at δ 4.55 (1H) and 4.75 (1H), and a vinylic methyl singlet at δ 1.71 (10–13), which agree with values expected for the protons of lupene derivatives. The ^{13}C-nmr spectrum of **1** also indicated the presence of five tertiary methyls and characteristic signals for an isopropylene [150.7 (C-20), 110.4 (C-29) 19.8 (C-30)] group.

Acid hydrolysis of **1** gave impressic acid [3α,11α-dihydroxylup-20(29)-en-28-oic acid] [**2**] (4,14), dehydroimpressic acid [3α-hydroxylup-9(11),20(29)-dien-28-oic acid] [**3**] (4), and D-glucose. Compound **3** was formed from **2** by dehydration of the 11α-OH group in acid (4,15).

Alkaline hydrolysis of **1** gave only impressic acid [**2**], which on treatment with Ac_2O/pyridine gave a diacetate **5**, identical in all respects with an authentic sample of 3α,11α-diacetylimpressic acid (4). These results indicated that **1** was a monodesmoside of **2** and the sugar units were attached to C-28 of the aglycone through an ester linkage. This conclusion was supported by the characteristic ^{13}C-nmr signals [175.3 (C-28) and 95.4 ppm (anomeric C-1)] for an ester type of glycosidic linkage (16).

Identification of the sugar unit was made from the eims fragmentation pattern of the peracetate **4** of **1**. Compound **4** exhibited peaks at *m/z* 331 and *m/z* 619 characteristic for terminal tetra-*O*-acetylglucose and tetra-*O*-acetylglucosyl-tri-*O*-acetylglucose moieties, respectively (17). This indicated that both sugar units were glucose. Careful analysis of the ^{13}C-nmr signals due to sugar part of **1** led to the identification of gentiobiose (18,19) as the sugar component of saponin **1**. Further confirmation regarding configuration of the sugar moieties were made from the ^{1}H- and ^{13}C-nmr spectra of **1**, which showed two anomeric protons (δ 5.03, doublet, $J = 7$ Hz; 6.25, doublet, $J = 7$ Hz) and two anomeric carbons at 95.4 and 105.3 ppm characteristic for β configuration of the glucopyranose units (8,18,19). Thus, **1** was characterized as 3α,11α-dihydroxylup-20(29)-en-28-oic acid 28-*O*-β-D-glucopyranosyl-(1↦6)-β-D-glucopyranoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. Ir spectra were taken with a Perkin-Elmer 399B spectrometer. ^{1}H- (80 MHz), and ^{13}C- (20 MHz) nmr spectra were measured with a Varian FT 80 A spectrometer. TMS was used as the internal standard, and chemical shifts were given in δ (ppm). Ms were determined on a JMXDX-300 spectrometer. Optical rotation was measured with a JASCO model DIP-181. Si gel 60–120 mesh (BDH) was used for cc, and Si gel G or H (Merck) was used for tlc, preparative tlc, and vlc. Spots were visualized by spraying with 10% H_2SO_4 followed by heating at 100°.

PLANT MATERIAL.—Plant material was collected from Darjeeling, India, and identified as *S. impressa* by Dr. S.P. Jain of the Botany Division. A voucher specimen (No. 1909) was deposited in the herbarium of this institute.

ISOLATION PROCEDURES.—Powdered air-dried stems and bark of *S. impressa* (2.3 kg) were extracted with MeOH at room temperature for 10 days. The extract was concentrated in vacuo and the residue was dissolved in H_2O. The H_2O solution was extracted with *n*-hexane, C_6H_6, $CHCl_3$, and EtOAc, and finally with *n*-BuOH saturated with H_2O. The *n*-BuOH fraction when concentrated under vacuum yielded a brown viscous mass (62.8 g), which was subjected to Si gel (725 g) cc and eluted with EtOAc with increasing amount of MeOH. Fractions (250 ml each) were collected and monitored by tlc. The EtOAc-MeOH (4:1↦7:3) eluate afforded a solid (0.39 g), which on further chromatographic separation over vlc followed by preparative tlc yielded **1** (0.27 g). The other eluates yielded saponins reported earlier (1–4).

Saponin **1**.—White powder (0.27 g): mp 268–270° (MeOH); $[\alpha]^{25}D$ +0.36 (MeOH, $c = 0.1$); ir ν max (KBr) cm^{-1} 3420, 2927, 1746, 1639, 1066, 900; ^{1}H nmr (CD_3COCD_3) δ 0.86, 0.95, 1.06, 1.15, 1.24 (S, Me-23, -24, -25, -26, -27), 1.71 (S, Me-30), 3.33 (brs, $W½ = 7$ Hz, H-3β), 3.60 (six-line pattern, $J = 11$ Hz, $J' = 5$ Hz, H-11β), 4.55 and 4.75 (2 × m, H_2-29), 5.03 (1H,

d, $J=7$ Hz, H-1″ of terminal glucose unit), 6.25 (1H, d, $J=7$ Hz, H-1′ of inner glucose unit); eims *m/z* [**e**]$^+$ 472 (2), [**e** − H_2O]$^+$ 454 (4), [**e** − $2H_2O$]$^+$ 436 (5), [**e** − H_2O − CO_2]$^+$ 392 (7), 285 (7), 246 (7), [**a**]$^+$ 237 (11), [**b**]$^+$ 234 (45), [**c**]$^+$ 219 (26), [**d**]$^+$ 152 (43), 147 (45), 135 (100), 121 (75), 107 (81); ^{13}C nmr (C_5D_5N) 36.0 (C-1), 27.0 (C-2), 75.5 (C-3), 38.7 (C-4), 49.8 (C-5), 19.8 (C-6), 36.4 (C-7), 43.0 (C-8), 56.4 (C-9), 40.1 (C-10), 70.1 (C-11), 38.5 (C-12), 37.0 (C-13), 43.3 (C-14), 30.3 (C-15), 32.6 (C-16), 57.2 (C-17), 47.4 (C-18), 49.8 (C-19), 150.7 (C-20), 31.2 (C-21), 37.7 (C-22), 30.0 (C-23), 23.2 (C-24), 18.0 (C-25), 17.1 (C-26), 15.1 (C-27), 175.3 (C-28), 110.4 (C-29), 19.8 (C-30), 95.4 (C-1′), 74.2 (C-2′), 78.4 (C-3′), 69.7 (C-4′), 78.1 (C-5′), 71.1 (C-6′), 105.3 (C-1″), 75.2 (C-2″), 78.7 (C-3″), 71.8 (C-4″), 78.4 (C-5″), 62.9 (C-6″).

Acid hydrolysis of saponin **1**.—A solution of saponin **1** (150 mg) in 10% aqueous HCl (6 ml) was heated on an H_2O bath for 5 h. The precipitate was filtered, washed with H_2O, and dried. Tlc of the aglycone [$CHCl_3$-MeOH (49:1)] showed it to be a mixture of two compounds which on preparative tlc yielded aglycone **2** (52 mg), mp 234–236° and ms *m/z* [M]$^+$ 472, and **3** (25 mg), mp 224–226° and ms *m/z* [M]$^+$ 454. Aglycones **2** and **3** were identified as 3α,11α-dihydroxylup-20(29)-en-28-oic acid [**2**] and 3α-hydroxylup-9(11),20(29)-dien-28-oic acid [**3**] on the basis of mp, ir, ^{1}H nmr, ^{13}C nmr, and co-tlc with authentic samples (4). The filtrate was neutralized with Ag_2CO_3 solution and the sugar identified as glucose by tlc.

Alkaline hydrolysis of saponin **1**.—A solution of **1** (80 mg) in 0.5 N aqueous KOH (5 ml) was heated on a boiling H_2O bath for 3 h. The precipitate was filtered, washed with H_2O, and dried (Na_2SO_4) to give aglycone **2** (40 mg) as the sole product, which was identical in all respects (mp, ir, ms, ^{1}H, ^{13}C nmr, and co-tlc) with an authentic sample. The filtrate, on neutralization with 0.5 N H_2SO_4, gave gentiobiose.

Peracetate **4** *of saponin* **1**.—A solution of **1** (15 mg) and Ac_2O/pyridine was allowed to stand at room temperature for 1 day. The crude product was chromatographed on Si gel to give **4** (14 mg): mp 250–252° (MeOH); ir *ν* max (KBr) cm^{-1} 1760, 1745, 1725 (ester), 1645 (>C=CH_2), 1240, 1220 (OAc); ^{1}H nmr ($CDCl_3$) δ 0.82, 0.88, 0.98, 1.14, 1.18 (S, Me-23, -24, -25, -26, -27), 1.58 (s, Me-30), 1.92, 2.00, 2.05 (OAc), 4.50 (brs, W½ = 7 Hz, H-3β), 4.50 and 4.62 (2 × m, H_2-29), 5.08 (six-line pattern, $J=11$ Hz, $J'=5$ Hz, H-11β), 5.62 (1H, d, $J=7$ Hz, anomeric H-1′ of glycosidic linkage), eims *m/z* [**f**] 619, [**e**]$^+$ 556, [**e**−HOAc]$^+$ 496, [**e**−2HOAc]$^+$ 436, [**g**]$^+$ 331, [**a**]$^+$ 321, 285, 246, [**b**]$^+$ 234, [**b**−H]$^+$ 233, [**c**]$^+$ 219, 201, 189, 175, 169, 161, [**d**]$^+$ 152 (Figure 1).

Acetylation of **2**.—A solution of **2** (40 mg) in Ac_2O/pyridine (1 ml) was allowed to stand at room temperature for 1 day. The crude product was chromatographed on Si gel to give diacetate **5** (30 mg), identical in all respects (mp, ir, ms, ^{1}H, ^{13}C nmr, and co-tlc) with an authentic sample.

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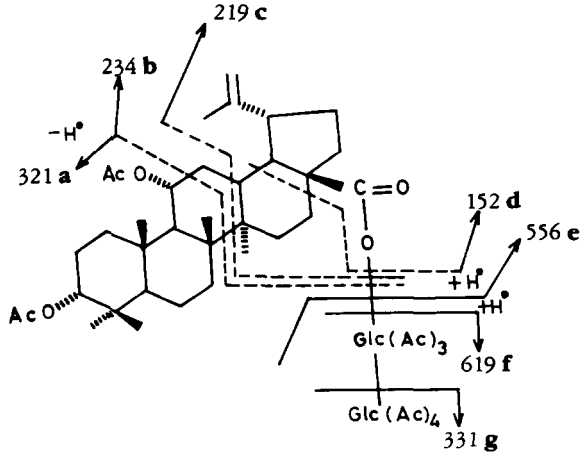

FIGURE 1. Eims fragmentation of **4**.

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