The proposed structure (**1**) as a diterpenoid furano lactone clearly satisfied the above spectral data The mass fragmentation pattern also supported the structure (**1**) The mass spectrum gave peaks at m/z 390 $[M]^+$, 346 $[M-CO_2]^+$, 95, 94 and 81 which are due to the fragments 'a', 'b' and 'c', respectively, in accord with similar diterpenoid furano lactones [4, 11] A characteristic and base peak at m/z 124 is assigned to the ion 'd' which arises by the retro-Diels–Alder type fragmentation of ring B

EXPERIMENTAL

Mps. uncorr. IR spectra were recorded in Nujol. The proton spin-decoupling NMR expts were carried out at 100 MHz

Extraction and isolation of (**1**). Stems of *T. cordifolia* Miers. (26 kg) were collected from IIT Campus, Bombay and identified by Dr. Agarkar, Institute of Science, Bombay. The stems were dried, finely powdered and extd with $CHCl_3$ (60 l) in a Soxhlet for 48 hr Repeated CC over silica gel with 70% EtOAc–petrol (60–80°) (7:3) afforded (**1**) which was recrystallized from MeOH (6·8 g, 3·8 × 10^{-3}%); as cubic crystals, mp. 231–233° (decomp.); $[\alpha]_D^{20} = +28.2$° (DMSO, c 0.62). IR ν_{max}^{nujol} cm^{-1} (Table 1), UV λ_{max}^{MeOH} log ε 207.8 nm (3.8). ^{1}H NMR (500 MHz, DMSO-d_6), (Table 2), ^{13}C NMR (125 MHz, DMSO-d_6), Table 4, MS. m/z 390 $[M]^+$ (0.5%), 346 $[M-CO_2]^+$ (1), 291 (1), 252 (25), 199 (2), 125 (24), 124 (100), 95 (38), 94 (32), 93 (12), 91 (25), 81 (33), Anal. calcd. for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.29; H, 5.54%.

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A SOYASAPOGENOL-B GLUCOSIDE FROM THE SEEDS OF *PHASEOLUS VULGARIS*

D. C. JAIN, R. S. THAKUR, A. BAJPAI* and A. R. SOOD*

Central Institute of Medicinal and Aromatic Plants, Lucknow 226016, India, *Sri G. S. Institute of Science and Technology, Indore 452001, India

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Key Word Index—*Phaseolus vulgaris* Leguminosae triterpenoid glucoside soyasapogenol B-24-*O*-β-D-glucopyranoside

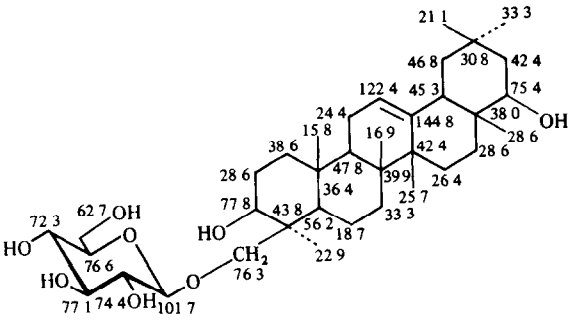
Abstract—A new triterpenoid glucoside has been isolated from the seeds of *Phaseolus vulgaris* and characterized as 3β,22β-dihydroxy olean-12-en-24-*O*-β-D-glucopyranoside

INTRODUCTION

Seeds of *Phaseolus vulgaris* Linn (French bean) are a rich source of saponins [1]. Crude extracts of the seeds show antifertility activity [2] and are known to contain phytosterols, triterpenoids and triterpenoid saponins [3–6]

RESULTS AND DISCUSSION

The new triterpenoid glucoside (**1**) was isolated from a methanolic extract of the seeds by column chromatography and purified by droplet counter current chromatography (DCCC)



1

The glucoside, $C_{36}H_{60}O_8$, exhibited broad bands at 3400 and 1050 cm^{-1} for hydroxy groups, and bands at 1650 cm^{-1} for a double bond. On Acid hydrolysis, it gave glucose (HPLC) and the aglycone **2**, $C_{30}H_{50}O_3$ (M^+, *m/z* 458), which was identified as soyasapogenol B (olean-12-en-3β,22β,24-triol) by IR, MS and ^{13}C NMR [7, 8]. Acetylation of **2** gave the triacetate **3**, $C_{36}H_{56}O_6$ (M^+, *m/z* 584; IR ν_{max}^{KBr} cm^{-1} 1740 and 1250)

Permethylation of **1** with 3% MeOH–HCl afforded a methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside [9] The ^{13}C NMR spectra of **1** showed one anomeric carbon signal at δ101.7 and suggested that **1** was a monoglucoside of soyasapogenol B [10]. Comparison of the ^{13}C NMR data of **1** with those of **2**) suggested that the glucose unit in **1** was linked to the C-24 hydroxy group of **2**. Thus the C-24 signal (δ76 3) in **1** was shifted downfield by δ11 7, compared with the other hydroxy-substituted carbons, C-22 (δ75.4) and C-3 (δ77.8). Due to C-24 glycosidation, the C-3 signal was shifted by δ2 4, while other carbon remained unaffected

The β-configuration of the glucose residue was assigned on the basis of the ^1H NMR signal of the anomeric proton (δ4 4; 1H, *d*, *J* = 8 Hz). The value of δ101.7 for the anomeric carbon signal was also indicative of a β-configuration [11] Based on the above observation the structure of **1** was assigned as 3β,22β-dihydroxyolean-12-en-24-*O*-β-D-glucopyranoside.

EXPERIMENTAL

Mps uncorr; DCCC DCC-A apparatus (Tokyo Rikakikai, Tokyo Japan).

Isolation of saponin The powdered seeds (500 g) of *P vulgaris*, were extracted with hexane followed by MeOH The MeOH extract was partitioned between H_2O and BuOH. The BuOH concentrate on addition of Me_2CO yielded a crude saponin (5 2 g) as a ppt The crude saponin (3 g) was subjected to CC on silica gel with $CHCl_3$–MeOH–H_2O (13·6 2). Fractions 20–25 (each 250 ml), each of which gave a single violet spot with other impurities on TLC, when sprayed with 10% H_2SO_4, were combined and further purified by DCCC [$CHCl_3$–MeOH–H_2O (7 13.8), lower phase as mobile phase (descending mode)] to afford a triterpenoid glucoside (**1**) (150 mg)

Compound **1**. Colourless crystals (MeOH), mp 278–280° (decomp), $[\alpha]_D$ +57°, R_f 0 30 ($CHCl_3$–MeOH–H_2O, 13 6 2) IR ν_{max}^{KBr} cm^{-1} 3400–3250 (OH), 2920, 2900, 2840, 1650 (C=C), 1460, 1380, 1050, ^1H NMR (pyridine-d_5) δ0 78, 0 84, 1 06, 1 14, 1 22, 1 36, 1 50 (*s* 7 × Me), 4 4 (1H, *d*, *J* = 8 Hz, H-1), 5 56 (1H, *br s* H-12), ^{13}C NMR. 1 Found C, 69 12, H9 23, $C_{36}H_{60}O_8$ requires C, 69 67 and H, 9 67

Hydrolysis of compound **1** Compound **1** (100 mg) was hydrolysed with 10% H_2SO_4 for 5 hr The usual work-up afforded **2** (72 2 mg), as colourless crystals ($CHCl_3$), mp 256–258°, $[\alpha]_D$ +89° ($CHCl_3$, C1), R_f 0 34 ($CHCl_3$–MeOH, 20 1), IR ν_{max}^{KBr} cm^{-1} 3400–3250 (OH), 2950, 2900, 1640 (C=C), 1465, 1380, 1045, MS *m/z* 458 $[M]^+$, 442, 440, 234 (base peak), 219, 216, 175, 161, 145, 133, ^{13}C NMR (pyridine-d_5) (C_1–C_{30}) 39 0, 28 4, 80 2, 43 2, 56 4, 19 0, 33 6, 40 0, 48 0, 37 0, 24 1, 122 4, 144 8, 42 4, 26 4, 28 6, 38 0, 45 0, 46 8, 30 8, 42 4, 75 6, 23 6, 64 6, 16 3, 17 0, 25 7, 28 6, 33 3, *and* 21 1

Acetylation of compound **2** Acetate **3** was prepared from **2** with Ac_2O and C_5H_5N and crystallized from ($CHCl_3$–MeOH), mp 177–178°, $[\alpha]_D$ +76° ($CHCl_3$, c1), IR ν_{max}^{KBr} cm^{-1} 2955, 1740 (CO), 1645, 1470, 1375, 1250, 1050, MS *m/z* 584 $[M^+]$ 524, 464, 404, 307, 276, 216 (base peak), 203, 187, 159, 145, 133

Sugar identification The aq hydrolysate from the hydrolysis of **1** was neutralized with $BaCO_3$ soln and the soln de-ionized The neutral sugar soln on examination by HPLC (carbohydrate column, flow rate 2 ml/min, EtOAc–EtOH–H_2O (13 8:2)), was found to contain glucose only

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