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A NEW TRITERPENOIDAL SAPONIN FROM *ACACIA AURICULIFORMIS*

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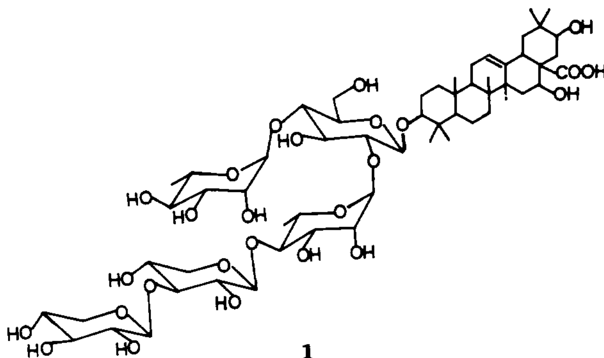
ABSTRACT.—A new triterpenoidal saponin has been isolated from an aqueous EtOH extract of the legumes of *Acacia auriculiformis* and characterized as 3-*O*-{[β-D-xylopyranosyl(1→3)-β-D-xylopyranosyl(1→4)-α-L-rhamnopyranosyl(1→2)]-[α-L-rhamnopyranosyl(1→4)]-β-D-glucopyranosyl}-3,16,21-trihydroxyolean-12-en-28-oic acid [**1**] by chemical studies and spectral data.

Acacia auriculiformis A. Cunn. (Leguminosae) is an Australian *Acacia* cultivated in India. *Acacia* is widely used as an indigenous drug in various ailments (1). The bark is a powerful astringent and the gum is used as a demulcent (1). Its bark contains tannin and the seeds contain a fatty oil (2). The EtOH extract of *A. auriculiformis* (aerial parts) was found (3) to have CNS depressant activity. The active constituent, a flavan glycoside named auriculoaside (4), exhibited CNS depressant activity. A number of flavonoids have been isolated (5) from the heartwood and bark of this plant, but no saponin has been reported to date. We now report a new triterpenoidal saponin from the legumes of *A. auriculiformis*.

Repeated cc of an aqueous EtOH extract of the defatted legumes of *A. auriculiformis* afforded **1**, which was identified as 3-*O*-{[β-D-xylopyranosyl(1→3)-β-D-xylopyranosyl(1→4)-α-L-rhamnopyranosyl(1→2)]-[α-L-rhamnopyranosyl(1→4)]-β-D-glucopyranosyl}-3,16,21-trihydroxyolean-12-en-28-oic acid. Compound **1** gave tests characteristic of a triterpenoidal saponin. Acidic hydrolysis of **1** furnished acacic acid along with the sugars D-glucose, D-xylose, and L-rhamnose in the ratio of 1:2:2 as determined by photocolorimetry (6). The molecular mass of **1** was deduced as 1206 by its fabms (negative ion) in which the molecular ion peak appeared at *m/z* 1205 $[M-H]^-$. Other peaks were recorded at *m/z* 1073 $[(M-H)-132]^-$ (pentose$-H_2O$), 1059 $[(M-H)-146]^-$ (deoxyhexose$-H_2O$), 927 $[(M-H)-(132+146)]^-$, 795 $[(M-H)-(2\times132+146)]^-$, 649 $[(M-H)-2\times(132+146)]^-$, 487 $[(M-H)-2\times(132+146)-162]^-$, indicating the sequence of sugars.

Hydrolysis of the permethylate of **1** prepared by Hakomori's method (7) afforded 2,3,4-tri-*O*-methyl-D-xylose, 2,3,4-tri-*O*-methyl-L-rhamnose, 2,4-di-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-L-rhamnose, and 3,6-di-*O*-methyl-D-glucose. The latter, 3,6-di-*O*-methyl-D-glucose, gave an intense pink color with



1

Wallenfel's reagent (8) indicating that it was not substituted in the 2 position. Partial hydrolysis of **1** afforded acacic acid and three prosapogenins. Interglycosidic linkages were confirmed by acidic hydrolysis and permethylation followed by acidic hydrolysis of these prosapogenins. Identification of the permethylated sugars was done by comparison with authentic samples (9,10). The ir of **1** was consistent with free 28-COOH and 21-OH groups. The type of linkages at glycosidic points and the positions of linkages were further confirmed by ^{1}H and ^{13}C nmr of **1**. Assignments of signals in nmr were made by comparison with reported data of acacic acid (11) and sugars (12).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were recorded with a Boetius microscopic apparatus. Fabms was obtained in the negative ion mode on a JEOL JMS HX-110 instrument using MeOH and glycerol as solvents. ^{1}H nmr was performed at 400 MHz, and ^{13}C nmr was done at 25 MHz. Cc was performed on Si gel (Merck, 60–120 mesh) and tlc on Kiesel gel 60G (Merck). Spots on tlc were visualized by spraying with 7% H_2SO_4 followed by heating. Pc was carried out on a Whatman No. 1 paper using the descending mode with visualization using aniline hydrogen phthalate. Colorimetric estimations were recorded on a type 103 Syntronic spectrophotometer.

ISOLATION.—The legumes (2 kg) of cultivated *A. auriculiformis* were collected from the Botanical Gardens of the Department of Botany, H.N.B Garhwal University, Srinagar and identified by Dr. A.B. Bhatt, Associate Professor, Department of Botany, H.N.B. Garhwal University, Srinagar. A voucher specimen is preserved in the Herbarium of the Botany Department. The air-dried and coarsely powdered legumes were defatted with petroleum ether. The defatted mass was exhaustively extracted with aqueous EtOH and concentrated under reduced pressure. The combined extract was fractionated through cc using $CHCl_3$-MeOH (85:15) to afford **1** (3 g).

COMPOUND **1**.—Crystallized from MeOH as colorless needles: mp 255–257°; ir max cm^{-1} 3660, 3490, 1710; fabms *m/z* 1205, 1059, 1073, 927, 795, 649, 487, 207, 190; ^{1}H nmr (in C_5D_5N) 5.62 (1H, d, J=6.8 Hz, anomeric proton of glucose), 5.18 (1H, br s, H-1, rhamnose), 4.92 (1H, s, H-1, rha'), 4.74 (1H, d, J=7.0 Hz, H-1, xylose), 4.65 (1H, d, J=7.5 Hz, H-1, xyl'); ^{13}C nmr (C_5D_5N) C-1–C-30 of aglycone 39.6, 27.8, 82.3, 39.3, 56.8, 17.9, 29.8, 39.9, 46.6, 37.6, 23.7, 122.3, 143.8, 41.8, 36.2, 73.9, 52.1, 40.2, 47.8, 27.9, 74.6, 36.8, 28.8, 17.2, 13.9, 17.6, 27.8, 182.4, 34.8, 19.8. Carbons of sugar moieties: C-1–C-6 of glucopyranosyl, 104.2, 79.2, 77.8, 75.3, 76.1, 61.6; C-1–C-5 of xylopyranosyl, 105.8, 75.1, 87.6, 69.2, 67.8; xyl' C-1–C-5 105.4, 74.8, 77.6, 71.2, 66.3; C-1–C-6 of rhamnopyranosyl 101.6, 71.4, 72.6, 83.6, 67.9, 18.7; rha' C-1–C-6 101.3, 71.6, 72.4, 74.1, 68.9, 18.1.

ACIDIC HYDROLYSIS OF **1**.—Compound **1** (30 mg) was refluxed with 2 N HCl-MeOH (1:1) (8 ml) on a boiling H_2O bath for 2.5 h to afford the aglycone (acacic acid), crystallized as colorless flakes: mp 273–275° [lit. (13) mp 275–276°], eims *m/z* $[M]^+$ 488. The neutralized (Ag_2CO_3) and concentrated aqueous hydrolysate showed the presence of D-glucose, D-xylose and L-rhamnose [pc solvent *n*-BuOH–HOAc–H_2O (4:1:5)]. R_f values 0.23, 0.28, and 0.36, respectively.

PARTIAL HYDROLYSIS OF **1**.—Compound **1** (200 mg) in 1 N HCl–*n*-BuOH (1:1) (20 ml) was heated at 70° for 3 h. The *n*-BuOH phase was washed with H_2O and evaporated to dryness in vacuo. The residue after cc [MeOH-$CHCl_3$ (1:9)] yielded acacic acid (10 mg), and 3 prosapogenins A (75 mg), B (30 mg), and C (35 mg).

ACIDIC HYDROLYSIS OF PROSAPOGENINS.—The prosapogenins A, B, and C (5 mg each) were hydrolyzed separately as above. The neutralized and concentrated hydrolysate from A gave D-glucose, D-xylose, and L-rhamnose; B gave D-glucose and L-rhamnose, and C afforded only D-glucose.

PERMETHYLATION STUDIES ON **1** AND PROSAPOGENINS.—Compound **1** (100 mg) and prosapogenins A, B, C (20 mg each) were separately permethylated with NaH and MeI (7), and the products were purified [cc, C_6H_6-Me_2CO (4:1)] to afford permethylethers. The permethylethers of **1** and the prosapogenins (15 mg each) were separately refluxed with 2 N HCl-MeOH (1:1) (5 ml) as above. The neutralized and concentrated hydrolysate from **1** showed [pc, *n*-BuOH–EtOH–H_2O, (5:1:4)] 2,3,4-tri-*O*-methyl-D-xylose, 2,3,4-tri-*O*-methyl-L-rhamnose, 2,4-di-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-L-rhamnose, and 3,6-di-*O*-methyl-D-glucose. The last permethylated sugar gave an intense pink color with Wallenfel's reagent. The hydrolysate of permethylated A gave 2,3,4-tri-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-L-rhamnose, and 3,4,6-tri-*O*-methyl-D-glucose; B gave 2,3,4-tri-*O*-methyl-L-rhamnose and 3,4,6-tri-*O*-methyl-D-glucose; and C afforded 2,3,4,6-tetra-*O*-methyl-D-glucose.

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