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IPOPURPUROSIDE, A NEW GLYCOSIDE FROM *IPOMOEA PURPUREA**

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Key Word Index—*Ipomoea purpurea*; Convolvulaceae; ipopurpuroside; ricinoleic acid.

Abstract—A new glycoside, ipopurpuroside, has been isolated from *Ipomoea purpurea*. The results of acid hydrolysis together with chemical and spectroscopic analyses have shown that it consists of glucose, rhamnose and 6-deoxy-D-glucose glycosidically linked to ricinoleic acid. The acyl group removed by alkaline hydrolysis was identified as methylbutyric acid. The carboxyl group of ipopurpuroside is esterified.

INTRODUCTION

The various plants of the Convolvulaceae contain a unique group of glycosides [1, 2]. When subject to acid hydrolysis these glycosides give hydroxylated fatty acids as aglycone and a mixture of aldohexoses [3, 4]. On alkaline hydrolysis they give short chain aliphatic acids and glycosidic acids. The aglycones and sugars most frequently obtained from Convolvulaceous glycosides are 11-hydroxyhexadecanoic acid [5], dihydroxy derivatives of tetradecanoic [6], hexadecanoic [7] and octadecanoic acids [8] and glucose, rhamnose, fucose and 6-deoxy-glucose [3, 4].

During an investigation of the seed of *Ipomoea purpurea* in an attempt to isolate the physiologically active alkaloids [9] two new glycosides were isolated. The present paper is concerned with the characterization of a glycoside which we propose to name ipopurporoside.

RESULTS AND DISCUSSION

From the seeds of *I. purpurea* a glycosidic mixture was obtained by extraction with ethanol. PC suggested that the isolated material was a mixture of two glycosides. The glycoside ipopurpuroside (mp 150°; R_f system 4, 0.55) was subject to structural analyses.

Elementary analyses of ipopurpuroside gave the empirical formula $C_{42}H_{74}O_{16}$ (MW 835). The IR spectrum showed absorption indicating the existence of a β-glycosidic bond. Acetylation gave a crystalline substance and a determination of the acetyl groups suggested the presence of 7 OH groups.

The IR spectrum of the acetate indicated complete acetylation. The ipopurpuroside gave a positive test with bromine water and hydroxylamine, but a negative test for acidity.

The aglycone obtained by hydrolysis with 3N HCl and its Me ester was identified by IR, TLC and GLC as ricinoleic acid. The elementary analyses also supported the conclusion that the aglycone is ricinoleic acid. Hydrolysis of ipopurpuroside with ethanolic KOH yielded a steam volatile acid and a glycosidic acid. Investigation by GLC showed that the steam volatile acid is Me butyric. The sugar fraction liberated under acid hydrolysis was shown to be a mixture of glucose, rhamnose and 6-deoxyglucose.

EXPERIMENTAL

Ipopurpuroside was isolated from the seed of *I. purpurea* DEI-246 grown in the nursery garden Mikulja near Smederevo (Yugoslavia) and supplied by 'SEME' Export–Import, Beograd. Mps were determined on a Kofler block and are uncorr. GLC analyses were carried out with a FID instrument. MW determinations were carried out using a Knauer MW apparatus in C_6H_6. For identification of aglycones and acids obtained on alkaline hydrolysis, TLC using Si gel was employed with the following eluants: 1, $CHCl_3$–MeOH (9:1); 2, C_6H_6–MeOH (19:3); 3, *n*-BuOH–HOAc–H_2O (4:1:5). Spray reagent: 0.025% methyl red in EtOH. For the identification of sugars PC was used with eluant 4, EtOAc–HOAc–H_2O (9:2:2). Spray reagent: $AgNO_3$–Me_2CO.

Isolation. Seed (500 g) was ground to powder and treated with petrol to eliminate oils. The defatted seeds were extracted with EtOH at room temp. for 24 hr. Most of the solvent was removed and the residue treated with dry Et_2O. The Et_2O insoluble yellow amorphous powder (1.6 g) had mp, 135°. PC suggested that the isolated material was a mixture of two glycosides (R_f system 4, 0.55; 0.75). The Et_2O insoluble fraction was dissolved in MeOH and pptd with dry Et_2O. The resulting white amorphous powder, mp 150°, when examined by PC showed a single spot (R_f System 4, 0.55). Elementary analyses (C, 60.41%; H, 8.93%; MW 835) gave empirical formula $C_{42}H_{74}O_{16}$. The IR showed strong absorption at 3.0 μm (OH), 5.8 μm (C=O) and 11.5 μm (β-glycosidic bond). Ipopurpuroside gave a positive test with Br_2 water and negative results for acidity but a positive hydroxamic acid test.

Acetylation. Ipopurpuroside (0.5 g) was dissolved in dry Py (3 ml) and excess of Ac_2O (4 ml) was added. The soln was allowed to stand 18 hr at room temp. and poured into cold H_2O. Recrystallization from MeOH gave needles, mp 86°. Anal. calc. for $C_{56}H_{88}O_{23}$: C, 59.54%; H, 7.85%; acetyl 27.84%. Found C, 59.56%; H 7.95%; acetyl 28.08%.

Acid hydrolysis. Ipopurpuroside (1 g) was refluxed with 30 ml of 3N HCl for 4 hr and the hydrolysate extracted with Et_2O (3 × 25 ml). The ether extracts were shaken with satd $NaHCO_3$ and the aq. layer acidified with dil. HCl. Re-extraction with Et_2O gave, after evapn, a liquid aglycone (0.2 g). The aq. layer was neutralized with $NaHCO_3$, extracted with EtOAc and reserved for the examination of the carbohydrate components.

Examination of aglycone. The Et_2O soln obtained after acid hydrolysis, after evapn to dryness, gave a liquid aglycone (0.5 g)

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bp 226°. The IR showed strong absorption at 3.0 μm (OH); 3.8 μm (CH_2) and 5.8 μm (C=O). Anal. calc. for. $C_{18}H_{34}O_3$: C, 72.54; H, 11.50%. Found: C 72.32%; H, 11.85%. The Me ester was prepared by treatment with CH_2N_2–Et_2O [10] and analysed by TLC on Si gel and by GLC on 5% SE-30 (1 m × 2 mm). A number of known acids and their Me esters were run under the same conditions. The R_t and R_f values for the aglycone were identical with those obtained from commercial ricinoleic acid (R_f System 1, 0.97; R_f System 2, 0.90; R_t 7.75 min).

Hydrogenation of aglycone. Aglycone (0.1 g) was dissolved in $CHCl_3$ (2 ml) and 5% palladium chloride on charcoal (0.5 g) was added. The aglycone absorbed 1 mole equivalent of H_2 in 4 hr. After the removal of solvent the liquid residue was identified by means of TLC as 12-hydroxystearic acid (R_f System 1 0.97).

Examination of carbohydrate components. The aq. layer obtained on acid hydrolysis was neutralized with $NaHCO_3$, extracted with EtOAc and evapd to dryness. PC indicated the presence of glucose, rhamnose and 6-deoxyglucose. To confirm these results the residue after evapn (10 mg) was dissolved in dry Py and TMSi ethers prepared by addition of hexamethyldisilazane (1 ml) and trimethylchlorosilazane (0.5 ml). The obtained mixture was separated on a 1 m × 2 mm column of 10% SE-30 operated at 150°, N_2 at 90 ml/min. The R_t (min) obtained for investigated TMSi derivatives corresponded to: α- and β-rhamnose 2.6 and 3, 6-deoxy-glucose 4.3, and α- and β-glucose 10.3 and 15.6: For the direct examination of carbohydrate, ipopurpuroside (2 mg) was hydrolysed with 3N HCl (25 ml) containing MeOH (5 ml) at 100° for 30 min. The reaction mixture was neutralized with $NaHCO_3$, extracted with EtOAc and evapd at room temp. under vacuum. The residue was dissolved in dry Py (0.5 ml) and the TMSi ethers prepared by the addition of hexamethyldisilazane (0.2 ml) and trimethylchlorosilazane (0.1 ml).

Alkaline hydrolysis. Ipopurpuroside (2 g) was refluxed for 1 hr with N KOH. The mixture was acidified with N HCl and extracted with $CHCl_3$. The $CHCl_3$ was removed and the residue subjected to steam distillation. The steam distillate was extracted with Et_2O which after evapn yielded a liquid acidic material (0.15 g). The acid obtained by steam distillation and its Me ester were analysed by TLC and GLC and identified as Me butyric acid (R_f System 1, 0.74; R_f System 2, 0.82; R_t 3 3 min)

Separation of glycosidic mixture by gel filtration. Isolated glycosidic mixture (10 g) was dissolved in EtOH (3–4 ml) and applied to a Sephadex LH-20 column (1 × 100 cm) with EtOH as eluent. Fractionated glycosides were identified by means of PC in solvent 4. Ipopurpuroside with R_f System 4, 0.55 was eluated after the glycoside with R_f System 4, 0 75

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