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TYROSINE *O*-GLUCOSIDE AND DOPAMINE 3-*O*-GLUCOSIDE IN SEEDS OF *ENTADA PURSAETHA*

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Abstract—L-Tyrosine *O*-glucoside (I) and dopamine-3-*O*-glucoside (II) have been isolated from seeds of *Entada pursaetha* DC. The structures have been established by spectroscopic methods, identification of hydrolysis products and comparison with synthetic material. Syntheses are described of II, dopamine 4-glucoside and tyramine-*O*-glucoside.

INTRODUCTION

IN CONTINUATION of a study of amino acids and amines in the Mimosaceae,[1] seeds of *Entada pursaetha* DC. were examined. *E. pursaetha* is a widely distributed climber with very large, polished flat circular seeds (av. dia. *ca.* 5 cm) (I). It belongs to a group of species which previously have been referred to as a single species, variously called *E. scandens* (L.) Benth., *E. gigas* (L.) Fawc. & Rendle, or *E. phaseoloides* (L.) Merr.[2] We now report the identification of L-tyrosine-*O*-glucoside and dopamine-3-*O*-glucoside (II) as major constituents in the seeds. The structures have been unequivocally established by comparison with synthetic material. A preliminary account of part of this work has been given previously.[3]

RESULTS

Paper chromatographic investigations of crude seed extracts of *E. scandens* revealed the presence of two unknown major constituents, which gave greyish-purple colours with ninhydrin indicative of phenylethylamine derivatives. Paper electrophoresis indicated that one was a neutral amino acid, the other an aliphatic amine. Isolation of both was accomplished by ion-exchange resins and cellulose columns.[4,5] The isolated compounds each constituted about 1·5% of the fresh weight of peeled seeds. The identity of the neutral amino acid as I was easily established by elementary analysis, spectroscopic methods; hydrolysis with either HCl or emulsin gave tyrosine and glucose. Final corroboration was

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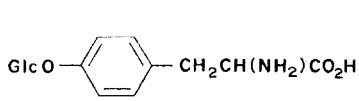
obtained by comparison with synthetic material.[6] The identity of the amine as a monoglucoside of 3',4'-dihydroxyphenylethylamine (dopamine) was again established by elementary analysis by spectroscopic methods and by hydrolysis to dopamine and glucose. Satisfactory yields of dopamine could only be obtained by performing the hydrolysis under nitrogen to avoid the formation of coloured oxidation products. The presence of a free phenolic group in the amine was demonstrated by the bathochromic shift in the UV spectrum (see Table 1).

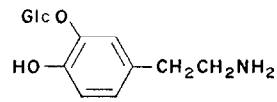
TABLE 1. UV SPECTRA OF AMINO ACID AND AMINE GLUCOSIDES

Compound	λ_{max} (nm) (log ϵ_{max}) Phosphate buffer pH 6·5	0·1 M NaOH
Tyrosine *O*-glucoside (I)	270 (3·0), 276 (2·9)	270 (3·0), 276 (2·9)
Dopamine 3-*O*-glucoside (II)	277 (3·2)	294 (3·3)
Dopamine 4-*O*-glucoside (III)	277 (3·3)	294 (3·5)
Tyramine *O*-glucoside (VI)	270 (3·0), 277 (2·9)	270 (3·0), 276 (2·9)
	in 96% EtOH	
Peracetate of II (IV)	270 (3·2), 276 (3·2)	
Peracetate of III (V)	272 (3·1), 277 (3·1)	

The position of the glucosyl group in the amine was established by synthesis of both II and dopamine-4-*O*-glucoside (III), from 4-benzyloxy-3-hydroxybenzaldehyde and 3-benzyloxy-4-hydroxybenzaldehyde.[7,8] Glucosylation was performed with α-D-tetraacetylglucopyranosylbromide to give 4-benzyloxy-3-(β-D-tetra-acetylglucopyranosyloxy)benzaldehyde (VII) and 3-benzyloxy-4-(β-D-tetra-acetylglucopyranosyloxy)benzaldehyde (VIII). Reaction with nitromethane yielded 4-benzyloxy-3-(β-D-tetra-acetylglucopyranosyloxy)-β-nitrostyrene (IX) and 3-benzyloxy-4-(β-D-tetra-acetylglucopyranosyloxy)-β-nitrostyrene (X).[9] Reduction with a large excess of $LiAlH_4$ resulted in debenzylation, reduction of the nitrostyrenes to the phenylethylamines[10] and loss of the *O*-acetyl groups. The isomers II and III were easily distinguished by chromatography and PMR spectroscopy (see Experimental) and the natural product was found to be identical to II. Further comparison was made of the peracetylated derivatives.



(I)



(II)

For comparative purposes, tyramine *O*-glucoside (VI) was synthesized using a procedure similar to that previously described for the synthesis of I,[6] involving *N*-carbobenzoxytyramine (XI), *N*-carbobenzoxy-*O*-(β-D-tetraacetylglucopyranosyl)tyramine (XII), and *N*-carbobenzoxy-*O*-(β-D-glucopyranoxyl)tyramine (XIII) as intermediates.

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DISCUSSION

I and II are new natural glucosides. A structurally related glucoside present in *Vicia faba* (Leguminosae) has been provisionally identified as dopa-3-*O*-glucoside.[11] An *O*-glucoside of mimosine (3-(3-hydroxy-4-oxo-l(4H)-pyridine)-L-alanine) has been isolated from *Mimosa pudica* L. and *Leucaena leucocephala* (Lam.) de Wit (Mimosaceae).[12] An enzyme has been partly purified from seedlings of *L. leucocephala* which is able to catalyse the synthesis of this glucoside from mimosine and UDP-glucose.[13] The same enzyme preparation is able to produce I from tyrosine and UDP-glucose, although at a very slow rate.[13] 2-(β-D-Glucopyranosyl)-4-(2-carboxy-2-aminoethyl)-3-isoxazolin-5-one has been isolated from *Pisum sativum* L. (Leguminosae),[14] 4-(β-D-Galactopyranosyloxy)-4-isobutylglutamic acid has recently been isolated from *Reseda odorata* L. (Resedaceae).[5]

The Mimosaceae have recently been screened for amino acids and amines, but the survey excluded the genus *Entada*.[15] Preliminary screening in this laboratory of seeds from *E. abyssinica* Steud. and *E. africana* Guill. et Perr failed to reveal the presence of either I or II. However, *E. gigas* (L.) Fawe & Rendle seeds contain II and *E. polystachia* (L.) DC. seeds contain VI.[16] *N*-acetyldopamine-4-*O*-glucoside, the *N*-acetyl derivative of III, has tentatively been identified in insects.[17,18] The glucoside is metabolically closely related to *N*-acetyldopamine, a key substance in schlerotinization of insect cuticle.[18]

TABLE 2. R_f OF AMINE ACID AND AMINE GLUCOSIDES

Compound	R_f (×100) in solvents* 1	2	3	4	5
Tyrosine *O*-glucoside	12	45	10	00	—
Dopamine 3-glucoside (II)	32	79	20	00	—
Dopamine 4-glucoside (III)	27	80	16	00	—
Tyramine *O*-glucoside	30	65	40	00	—
Tyrosine	40	60	23	00	—
Tyramine	55	90	75	10	—
Dopamine	45	—	—	03	—
Peracetate of II	—	—	—	65	50
Peracetate of III	—	—	—	54	44

* *Key:* 1, BuOH–HOAc–H_2O (12:3:5); 2, PhOH–H_2O–conc. NH_3 (120:30:1) (w/v/v); 3, *iso*-PrOH–conc. NH_3–H_2O (8:1:1); 4, Et_2O–EtOH (7:1); 5, EtOAc–EtOH (7:1). Solvents 1–3 on paper by descent, solvents 4 and 5 on silica gel plates.

EXPERIMENTAL

General methods. UV spectra are collected in Table 1; R_f data in Table 2. IR spectra were determined in KBr. For the PMR spectra, chemical shifts are in ppm relative to TMS in $CDCl_3$ and to sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate in D_2O; *J* values in Hz. Microanalyses were performed by Mr. G. Cornali, Copenhagen.

Isolation of (I) *and* (II). The seeds of *Entada pursaetha* DC. were provided by Professor A. Kjaer, Institute of Organic Chemistry, Technical University of Denmark, who in turn received them from Professor R. T. Govindachari, CIBA Research Centre, Bombay, India. After mechanical crushing of the shell the peeled seeds (480 g) were homogenized in CCl_4 and defatted twice with CCl_4 (2·5 l. portions) by refluxing (7 hr),

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cooling and filtration. The air-dried residue (429 g) was extracted 3× with MeOH–H_2O (7:3, 2·5 l. each time) by refluxing (5 hr), cooling and filtration. The combined filtrates were concentrated to dryness (176 g). The residue was suspended in H_2O (0·5 l.), filtered and applied to Amberlite IR 120 (H^+, 5 × 80 cm). The latter was washed with H_2O (7 l.), and the amino acids were eluted with aq. NH_3 (2N, 5 l.). The eluate was evaporated to dryness (17 g) and the residue was dissolved in H_2O and applied to Amberlite IRA 400 ($MeCOO^-$, 2·5 × 40 cm). The column was washed with H_2O and the eluate consisting of the neutral and basic amino acids and amines concentrated to give a yellow semisolid (14·2 g). The residue was dissolved in H_2O (20 ml) and applied to Dowex 50W ×8 (200–400 mesh, NH_4^+, 1·5 × 75 cm). The column was rinsed with H_2O (1·5 l.) and eluted with aq. NH_3 (1 N). The effluent was collected in fractions of 15 ml. Fractions 4–30 contained I and small amounts of other neutral amino acids, fractions 101–120 contained II and small amounts of other basic compounds. Fractions 4–30 were combined and evaporated to dryness yielding a semicrystalline residue of I (7·9 g). Crystallization from EtOH–H_2O gave I as colourless needles (m.p. 281° (decomp.), lit.[6] 282° (decomp.)). $[\alpha]_D^{20}$ −62·5° (*c* 1·3, 0·1 N HCl), $[\alpha]_{546}^{20}$ −77° (*c* 1·3, 0·1 N HCl), lit.[6] $[\alpha]_{546}$ −77° (*c* 1, 0·1 N HCl). (Found: C, 52·21; H, 6·25; N, 4·06. Calc. for $C_{15}H_{21}NO_8$: C, 52·46; H, 6·17; N, 4·08%.) The PMR spectrum of I in D_2O showed the anomeric proton at 5·1 ppm (*J* 6 Hz), the remaining protons from the carbohydrate part in a complex pattern at 3·3–4·2 ppm, the aromatic protons in two doublets at 7·20 and 7·45 ppm, (*J* 9 Hz), the α-proton in the amino acid part at 4·4 ppm and the benzylic protons at 3·30 ppm. IR ν_{max}^{KBr} 3385 cm^{-1} (strong), 3200(s), 1605(s), 1580(s), 1505(s), 1450 (medium), 1435(m), 1415(m), 1360(s), 1325(s), 1245(s), 895(m), 880(m), 840(m), 800(m), 740(m), 650(m), 575(m), 530(m). I synthesized according to the lit[6] was identical with the isolated material (IR, UV, PMR spectra, m.m.p., co-chromatography). Fractions 101–120 were combined and evaporated to dryness leaving a semicrystalline, brown residue of II (6·4 g). Further purification of II (4·2 g) was accomplished by use of a cellulose column (2 × 50 cm) with *n*-BuOH–HOAc–H_2O (12:3:5). The effluent was collected in 10 ml fractions. Fractions 12–25 containing II were combined and evaporated to dryness leaving the semicrystalline acetate of II (3·4 g). Final purification was obtained by passage of the acetate through Dowex 1 × 8, (200–400 mesh, $MeCOO^-$, 2·5 × 100 cm) and a charcoal column (1·2 × 3 cm). The eluate from the last column by evaporation yielded the colourless crystalline acetate of II (1·6 g), $[\alpha]_D^{20}$ −53·8° (*c* 2, H_2O). (Found: C, 49·91; H, 6·76; N, 3·84. $C_{16}H_{25}NO_9$ required: C, 51·19, H, 6·71, N, 3·73%.) The free amine II was liberated from the acetate by use of Dowex 50W ×8 (200–400 mesh, NH_4^+, 1 × 10 cm). II, bound to the column, was eluted with aq. NH_3 (1 N). Concentration of the NH_3 eluate yielded II as a semicrystalline brown residue, $[\alpha]_D^{20}$ −62·0° (*c* 2, H_2O). (Found: C, 51·94; H, 6·76; N, 4·66. $C_{14}H_{21}NO_7$ required: C, 53·33; H, 6·71; N, 4·44%.) The PMR spectrum of II in D_2O showed the protons from the carbohydrate portion in a pattern similar to that found for I. Two aromatic protons were positioned at 6·9 ppm (*J* < 2 Hz), one aromatic proton at 7·1 ppm (*J* < 2 Hz), two protons from the ethyl group occurred at 2·8 ppm and the other two at 3·2 ppm in a pattern similar to that of dopamine itself.

N-*Acetyl*-2-(4-*acetoxy*-3-(β-D-*tetra-acetylglucopyranosyloxy*)*phenyl*) *ethylamine* (IV) *from natural* II. Peracetylation of natural II (2·17 g) was performed by a previously described method.[4] The product (3·04 g, 88%) was purified by chromatography on a silica gel column with EtOAc–EtOH (7:1), and on a charcoal column with $CHCl_3$. Evaporation of the final eluate gave colourless IV, $[\alpha]_D^{20}$ −16° (*c* 3·6, 96% EtOH), $[\alpha]_D^{20}$ +0·7° (*c* 5, $CHCl_3$). (Found: C, 54·28; H, 6·00; N, 2·34. $C_{26}H_{33}NO_{13}$ required: C, 55·02; H, 5·86; N, 2·47%). The PMR spectrum of IV in $CDCl_3$ showed the 18 protons from the 6 acetyl groups as singlets at 1·9–2·2 ppm, the two benzylic protons at 2·8 ppm and the two protons in the CH_2–N–group at 3·4 ppm, the three aromatic protons in one peak at 6·95 ppm, the amide proton at 5·8 ppm and the carbohydrate protons at 3·9 ppm (H_5), 4·2 ppm (two H_6) and 4·8–5·5 ppm (H_1, H_2, H_3, H_4). IR ν_{max}^{KBr} 3400 cm^{-1} (s), 2940 (m), 1760 (s), 1660 (s), 1660 (w), 1540 (m), 1510 (s), 1430 (m), 1370 (s), 1230 (s), 1165 (w), 1120 (m), 1040 (s), 900 (s), 830 (m).

4-*Benzyloxy*-3-(β-D-*tetra-acetylglucopyranosyloxy*)*benzaldehyde* (VII). 4-Benzyloxy-3-hydroxybenzaldehyde[8] (11·5 g) and α-D-tetra-acetylglucopyranosylbromide (22·5 g) in acetone (200 ml) were mixed with KOH (4 g) in H_2O (10 ml) and stirred for 5 hr at room temp. The reaction mixture was poured onto ice, and VII was isolated by filtration and recrystallization from 96% ethanol. Colourless crystals (from EtOH) (10 g, 36%) were obtained (m.p. 143° (lit.[19] 141–2°)). $[\alpha]_D^{20}$ −48·5° (*c* 2·4, acetone). (Found: C, 60·14; H, 5·36. Calc. for $C_{28}H_{30}O_{12}$: C, 60·21; H, 5·42%.)

3-*Benzyloxy*-4-(β-D-*tetra-acetylglucopyranosyloxy*)*benzaldehyde* (VIII). VIII was obtained as described for VII from 3-benzyloxy-4-hydroxybenzaldehyde[7] (4·4 g). Colourless crystals (6·4 g, 60%) were obtained (m.p. 133°). $[\alpha]_D^{20}$ −58·0° (*c* 2, acetone). (Found: C, 60·11; H, 5·60%.)

4-*Benzyloxy*-3-(β-D-*tetra-acetylglucopyranosyloxy*)-β-*nitrostyrene* (IX). A solution of VII (10 g), nitromethane (10 ml), and ammonium acetate (4 g) in HOAc (40 ml) was refluxed for 2 hr and poured into ice. IX was isolated by filtration and recrystallization from acetone–EtOH (4:1). Yield 7·1 g (66%), m.p. 188–190°. $[\alpha]_D^{20}$ −18·8° (*c* 2·1, $CHCl_3$). (Found: C, 58·02; H, 4·97; N, 2·28. $C_{29}H_{31}NO_{13}$ required: C, 57·88; H, 5·20; N, 2·33%.)

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3-*Benzyloxy*-4-(β-D-*tetra-acetylglucopyranosyloxy*)-β-*nitrostyrene* (X). X was obtained from VIII as described for IX. Yield 4·2 g from 4·5 g of VIII (87%), m.p. 180–183°. $[\alpha]_D^{20}$ −58° (*c* 3·6, $CHCl_3$). (Found: C, 58·00; H, 5·28; N, 2·08%.)

II *from* IX. IX (6·8 g) was refluxed with $LiAlH_4$ (25 g) in tetrahydrofuran (500 ml) for 72 hr. Excess $LiAlH_4$ was destroyed with H_2O and the filtered reaction mixture was applied to a strongly acid ion-exchange resin (Dowex 50W ×8, 200–400 mesh, NH_4^+, 1·5 × 75 cm). II was isolated from the NH_3 eluate of the column as described for natural II. A brown semicrystalline solid (3·5 g, 100%) was obtained. $[\alpha]_D^{20}$ −52° (*c* 3·7, H_2O). UV and PMR spectra were identical with those obtained for natural II. The identity was further established by co-chromatography in several systems (see Table 2).

2-(4-(β-D-*Glucopyranosyloxy*)-3-*hydroxyphenyl*)*ethylamine* (III). III was produced from X (6·8 g) as described for II. A brown semicrystalline solid (3·5 g, 100%) was obtained. $[\alpha]_D^{20}$ −66° (*c* 2, H_2O). The PMR spectrum of III in D_2O deviated from that of II only in the pattern for the 3 aromatic protons. One of these, protons occurred at 7·1 ppm (*d*, *J* 8 Hz), the second at 6·75 ppm (*d*, *J* 2 Hz), and the third at 6·55 ppm (*dd* *J* 8 and 2 Hz).

IV *from synthetic* II. The synthesis was performed as described for the natural material from synthetic II (0·84 g). Yield 1·3 g (86%). $[\alpha]_D^{20}$ −16° (*c* 2·1, 96% EtOH), $[\alpha]_D^{20}$ +0·5° (*c* 5, $CHCl_3$). (Found: C, 54·36; H, 5·87; N, 2·48%.) UV, IR and PMR spectra were identical with those obtained from IV derived from natural II. The identity was further established by co-chromatography (see Table 2).

N-*Acetyl*-2-(3-*acetoxy*-4-(β-D-*tetra-acetylglucopyranosyloxy*)*phenyl*)*ethylamine* (V). The synthesis was performed from III as described for II. Recrystallization from isopropanol provided colourless crystals, m.p. 123–126°. $[\alpha]_D^{20}$ −23·6° (*c* 3·3, 96% EtOH). $[\alpha]_D^{20}$ −10·3° (*c* 6, $CHCl_3$). (Found: C, 54·40; H, 5·89; N, 2·43%.) The PMR spectrum of V in $CDCl_3$ deviated from that of IV only in the pattern for the three aromatic protons. One of these protons occurred at 6·9 ppm ($J < 2$ Hz), the remaining two at 7·1 ppm ($J < 2$ Hz). The IR spectrum of V was similar to that of IV except for lack of bands at 1600 and 1165 cm^{-1} and additional bands at 3300 cm^{-1} (strong,) 925 (weak), 890 (s), and 800 (medium).

N-*Carbobenzoxytyramine* (XI). Carbobenzoxychloride (17 g) and Na_2CO_3 (2 N, 50 ml) were added to a mixture of tyramine (9 g) in $CHCl_3$ (100 ml) and water (50 ml). After stirring for 2 hr excess of HCl was added. XI was transferred to $CHCl_3$, then to 1 N NaOH and after acidification again to $CHCl_3$. After drying the extract was concentrated to yield crystalline XI (6·6 g), m.p. 99–100°. (Found: C, 70·67; H, 6·32; N, 5·12. $C_{16}H_{17}NO_3$ required: C, 70·81; H, 6·32; N, 5·16%.)

N-*Carbobenzoxy*-O-(β-D-*tetra-acetylglucopyranosyl*)*tyramine* (XII). To a mixture of XI (5·4 g), α-D-tetra-acetylglucopyranosylbromide (12·3 g), and quinoline (15 ml) in a mortar was added Ag_2CO_3[r](10·5 g).[6] After 2 hr, HOAc (75 ml) was added, the suspension centrifuged, and the supernatant poured into ice. After 16 hr at 0° XII was isolated by filtration and recrystallized from EtOH (5·4 g, 45%), m.p. 87–88°. $[\alpha]_D^{20}$ −16·2° (*c* 2, acetone). (Found: C, 59·52; H, 5·90; N, 2·32. $C_{30}H_{35}NO_{12}$ required: C, 59·88; H, 5·87; N, 2·33%.)

N-*Carbobenzoxy*-O-(β-D-*glucopyranosyl*)*tyramine* (XIII). XIII was obtained from XII (2 g) by reflux with NaOMe in MeOH.[20] Yield 1·5 g (100%), m.p. 148°. $[\alpha]_D^{20}$ −36·0° (*c* 2·9, 96% EtOH). (Found: C, 61·58; H, 6·43; N, 3·23. $C_{22}H_{27}NO_8$ required: C, 60·94; H, 6·28; N, 3·23%.)

O-(β-D-*Glucopyranosyl*)*tyramine*, HCl (*hydrochloride of VI*). XIII (1·1 g) was hydrogenated in 50% EtOH solution with a few drops AcOH and with Pd-black as catalyst.[6] Addition of excess HCl precipitated the crystalline hydrochloride of VI, (0·96 g, 88%), m.p. 180–182° (decomp.). $[\alpha]_D^{20}$ −55° (*c* 2·3, H_2O). (Found: C, 49·55; H, 6·76; N, 4·04; Cl, 11·07. $C_{14}H_{22}NO_6Cl$ required: C, 50·09; H, 6·61; N, 4·17; Cl, 10·55%.) The PMR spectrum of the hydrochloride in D_2O showed the aromatic protons and the carbohydrate protons in the same pattern and at the same δ-values as described for I and the protons in the ethyl group in the same pattern and at the same δ-values as described for II. IR ν_{max}^{KBr} 3350 cm^{-1} (strong), 2900 (s), 1620 (s), 1595 (weak), 1520 (s), 1470 (w), 1420 (w), 1320 (w), 1300 (w), 1235 (s), 1185 (medium), 1120 (m), 2070 (s), 1040 (s), 1020 (m), 900 (m), 850 (w), 825 (m), 790 (w), 775 (w), 655 (w), 630 (w), 620 (w), 550 (w), 510 (w).

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