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AN ANTHRAQUINONE 3-NEOHESPERIDOSIDE FROM *CASSIA SOPHERA* ROOT BARK

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Key Word Index—*Cassia sophera*; Leguminosae; 1,8-dihydroxy-2-methylanthraquinone 3-neohesperidoside.

Abstract—A new anthraquinone diglycoside has been isolated from *Cassia sophera* root bark and characterized as 1,8-dihydroxy-2-methylanthraquinone 3-neohesperidoside along with sitosterol, chrysophanol and physcion.

INTRODUCTION

Cassia sophera L. is well known for its medicinal value [1]. In a previous communication we have reported the presence of two anthraquinones in the root bark of this plant [2]. We now report the isolation and characterization of a new anthraquinone diglycoside.

RESULTS AND DISCUSSION

From the petrol fraction of the root bark of *C. sophera* three known compounds (sitosterol, chrysophanol and physcion) and one new compound (compound **4**) were isolated and characterized. Compound **4** analysed for $C_{27}H_{30}O_{14}$. It gave a positive Molisch test, but neither reduced Fehling's solution nor gave a purple colour with AHP reagent [3]. On acid hydrolysis it yielded an aglycone and two sugars identified as L-rhamnose and D-glucose by direct comparison with authentic samples.

The aglycone, $C_{15}H_{10}O_5$, gave characteristic colour tests for anthraquinones. Its λ_{max} and IR spectrum supported the presence of an anthraquinone ring system. A strong peak at 1450 cm^{-1} in the IR [4], a signal at δ2.38 in the ^1H NMR [5] and the formation of 2-methyl anthracene on Zn-dust distillation showed the presence of a β-methyl group. This was located at C-2 because the presence in the ^1H NMR of signals at δ7.35 (proton at C-7), δ7.52 (proton at C-4), δ7.72 (proton at C-6), δ7.96 (proton at C-5) established that positions 4, 5, 6 and 7 were unsubstituted. A peak at 3350 cm^{-1} in the IR and blue-green colour with alcoholic $FeCl_3$ indicated the presence of at least one free phenolic hydroxyl group. The formation of a triacetate of the aglycone established the presence of three such groups. An alcoholic solution of the compound formed a complex with copper sulphate showing the presence of a hydroxyl function α to a carbonyl group [6]. Its λ_{max} at 430 nm indicated the presence of at least two α-hydroxyl groups. Two strong peaks in the IR spectrum at 1675 and 1625 cm^{-1} and positive colour tests with alkali and formamide [7] and alkaline zirconium nitrate [8] confirmed the presence of the 1,8-dihydroxy system.

When the paper chromatogram of the aglycone was developed by spraying with 0.5% methanolic magnesium acetate and heating to 100° for 10 min, a pink colour was obtained indicating the presence of two hydroxyl groups at 1,3-positions [9]. The presence of a β-hydroxy group was further supported by its solubility in sodium carbonate [10]. Hence the aglycone was characterized as 1,3,8-trihydroxy-2-methylanthraquinone. It was confirmed by direct comparison with an authentic sample (mmp, co-TLC, superimposable IR) [11].

Both glycoside and aglycone gave positive tests for the 1,8-dihydroxy system while the test for the 1,3-dihydroxy system was given only by the aglycone. A strong maximum at 432 nm in the UV spectrum of the glycoside indicated the presence of at least two α-hydroxyls. This was confirmed by completely methylating the glycoside followed by hydrolysis, when the aglycone thus obtained gave a positive test only for β-hydroxyl. Both the sugars were in the pyranose form since periodate oxidation consumed 3 mol periodate with the liberation of 1 mol formic acid/mol glycoside. Mild acid hydrolysis with 1% sulphuric acid showed rhamnose to be the terminal sugar. The inter sugar linkage was confirmed as the neohesperidoside ($1 \rightarrow 2$) type by ^1H NMR (doublet at δ1.3 due to rhamnose methyl group) [12, 13]. This was further confirmed by hydrolysis of the permethylated glycoside to give two methylated sugars identified as 3,4,6-tri-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-L-*O*-rhamnose using 2,3,4,6-tetra-*O*-methyl-D-glucose as reference (paper chromatography; solvent BAW, 4:1:5, v/v upper phase: spray AHP, RG values 0.79 and 1.01). Hydrolysis of the glycoside with takadiastase liberated rhamnose whilst complete hydrolysis with almond emulsin gave glucose. This established the α-nature of the rhamnose and the β-nature of the glucose.

EXPERIMENTAL

Air dried plant material was supplied by United Chemical and Allied Products, Calcutta, India. Mps are uncorr. and were recorded on an electrically heated plate. TLC was done on silica gel G. The powdered root bark of *C. sophera* was extracted with hexane and Me_2CO successively. The concd Me_2CO extract was then fractionated into petrol, Et_2O, EtOAc and MeOH soluble portions. The petrol fraction yielded four compounds.

Compound **1**. Sitosterol, mp 130°, mmp 130°; acetate, mp 126°; digitonide, mp 128°.

Compound 2. Chrysophanol, mp 193°, mmp 194°; UV λ_{max}^{EtOH} nm: 229, 257, 267, 281 and 430.

Compound 3. Physcion, mp 205°, mmp 206°; UV λ_{max}^{EtOH} nm: 256 (sh), 266, 288, 431.

Compound 4. Orange yellow crystals, mp 196°, $C_{27}H_{30}O_{14}$ (Found C, 55.95%; H, 5.01%. Requires C, 56.05%; H, 5.19%). UV λ_{max}^{EtOH} nm: 240, 285 and 432; ^{1}H NMR (90 MHz, $CDCl_3$): δ1.30 (*d*, J = 6 Hz, 3H, Rha-Me), 2.35 (*s*, 3H, Me), 3.6 (*br*, sugar protons), 4.20 (*s*, 1H, H-1″ rhamnosyl), 5.10 (*br*, H-1‴ glycosyl), 7.38 (*d*, J = 8 Hz, 1H, C-7), 7.4 (*t*, J = 8 Hz, 1H, C-6), 7.54 (*s*, 1H, C-4), 7.98 (*d*, J = 8 Hz, 1H, C-5). Permethylation of the glycoside was carried out using 10% NaOH and DMS by the standard method. Completely methylated glycoside crystallized from Me_2CO–Et_2O mixture, mp 168° (found OMe, 35.85%, requires OMe, 35.94%). *Aglycone*: bright yellow crystals, mp 230°, $C_{15}H_{10}O_5$ [found C, 66.45%; H, 3.60%, requires C, 66.66%; H, 3.70%]; UV λ_{max}^{EtOH} nm: 220, 245, 255, 275, 280 and 430; IR ν_{max}^{KBr} cm^{-1}: 3350, 1700, 1675, 1625, 1575, 1550, 1450, 1375 and 1325; ^{1}H NMR (90 MHz, $CDCl_3$): δ2.38 (*s*, 3H, Me), 7.35 (*d*, J = 8 Hz, 1H, C-7), 7.52 (*s*, 1H, C-4), 7.72 (*t*, J = 8 Hz, 1H, C-6), and 7.96 (*d*, J = 8 Hz, 1H, C-5). *Triacetate*: Ac_2O and C_5H_5N at room temp., mp 205° (found Ac, 32.52%: $C_{15}H_7O_5(Ac)_3$ requires 32.57%). Zn-dust distillation was carried out using standard method. The crude bluish green product crystallized from C_6H_6, mp 204° (lit. 207°).

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