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SHORT REPORTS

IDENTIFICATION OF *p*-AMINOPHENYL-α-D-GLUCOSE FROM *HYDRANGEA MACROPHYLLA*

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Key Word Index—*Hydrangea macrophylla*; Saxifragaceae; *p*-aminophenyl-α-D-glucose.

While studying the chemical constituents of *H. macrophylla* leaves, a UV absorbing and aniline phthalate [1] positive compound was isolated. This compound has mp 158.5–159.5°, $[\alpha]_D^{20}$–62.5°, $C_{12}H_{19}NO_7$, and was positive to *p*-dimethylaminobenzaldehyde reagent [2] but negative to both a phenolic reagent [3] and a pyridine reactive reagent [4]. Hydrolysis with 0.1 N HCl gave glucose. Thus the compound is a derivative of aminophenol and glucose. The mass spectrum of the acetylated compound [5] showed M at m/e 481 which corresponds to $C_{12}H_{12}NO_6$ $(MeCO)_5$. As this compound was not hydrolyzed by emulsin but easily hydrolyzed by maltase, the combination of aminophenol and glucose must be of the α-type. The NMR spectrum in CD_3OD showed (δ in ppm), four doublets (7.07(2H), 6.87(2H), 5.82(1H), 4.20(2H) and one multiplet (3.90–3.60(4H)). The two bands (7.07 and 6.87) with a coupling constant of 6 Hz respectively were attributable to the four protons attached to a *p*-substituted benzene ring, which indicated that the aminophenol moiety in the molecule is *p*-substituted. The other three bands (5.82, 4.20 and 3.90–3.60) closely resembled to those of the characteristic signals of glucose and glucosides. The small coupling constant (1.7 Hz) of the 5.82 doublet is in good agreement with that of C_2 proton in α-glucosides [6], which also ascertained the glucoside linkage to be α-type. The doublet at 4.20 is due to C_6 proton and the multiplet at 3.60–3.90 is due to the protons attached to C_2, C_3, C_4 and C_5. Thus the isolated compound is *p*-aminophenyl-α-D-glucose, a new natural substance. Final confirmation of the structure was attained by comparing the isolated compound with the synthetic one. The IR, UV and NMR spectra, m.p. and m.m.p. and the optical rotation of the synthetic compound were identical with those of the isolated one.

EXPERIMENTAL

Isolation. Three kg of fresh leaves of *H. macrophylla* (Seringe) var. *thunbergii* (Makino) were homogenized and extracted with 5 vol 75% methanol. The aq residue obtained after evaporation of MeOH was extracted with *n*-BuOH (4 × 200 ml). The soln was concentrated *in vacuo* to dryness. Residue (16.81 g) was dissolved in 100 ml H_2O and filtered. Filtrate was applied to a Sephadex G-10 column and eluted with H_2O. Fractions containing a UV absorbing and aniline-phthalate positive compound were combined and it was evaporated *in vacuo* to dryness. The obtained yellow solid was recrystallized 2× from MeOH, giving needles (mp 155.5–156.5°). The aq soln of this compound was passed through a column of Dowex 50 × 4 (H^+ form) and the cations attached were eluted with 1N-aq NH_3. The eluate was concentrated *in vacuo* and residue recrystallized from MeOH giving needles (100 mg); mp 158.5–159.5°; $(\alpha)_D^{20}$-62.5° (C=0.5 in MeOH), UV; λ_{max} 300 nm $\epsilon = 789.0$ (EtOH); Found: C, 49.95%; H, 6.63%; N, 4.93%; Calcd for $C_{12}H_{17}NO_6$ H_2O; C, 49.80%; H, 6.69%; N, 4.93%.

Synthesis. Tetraacetyl-*p*-nitrophenyl-α-D-glucose [7] was reduced to tetraacetyl-*p*-aminophenyl-α-D-glucose according to the method of Latham *et al.* [8], which was hydrolyzed to *p*-aminophenyl-α-D-glucose [9].

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