Phytochemistry, 1974, Vol. 13, pp. 1998 to 1999. Pergamon Press. Printed in England.

CYANIDIN-3-ARABINOSYLSAMBUBIOSIDE IN *VIBURNUM TRILOBUM*

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(*Received* 18 *March* 1974)

Key Word Index—*Viburnum trilobum*; Caprifoliaceae; new anthocyanin; cyanidin 3-arabinosyl-sambubioside.

Cyanidin 3-arabinosylglucoside, a new pigment representing a sixth class of 3-bioside, was recently reported[1] to occur in *Viburnum trilobum* L. The identity of this pigment was confirmed and also found in appreciable quantities in *V. dentatum* L.[2] In the original *Viburnum trilobum* cultivar cyanidin 3-arabinosyl-glucoside was first isolated, there was no cyanidin 3-triglycoside.[2] However, in a different cultivar of *V. trilobum* L., cyanidin 3-xylosylrutinoside was found to be present as one of the major pigments. A minor pigment, inseparable from cyanidin 3-xylosylrutinoside in aqueous acid solvents, but clearly resolved on BFW chromatograms was detected.

The purified pigment showed similar chromatographic mobilities to cyanidin 3-xylosylrutinoside in aqueous acid solvents, but distinctly different, and slower, mobilities in butanolic based solvent systems (R_f in 1% HCl, 50; HOAc–HCl, 70; BAW, 18; $R_{Cy\text{-}3\text{-}G}$ in BFW, 26). It exhibited spectral properties typical of a cyanidin 3-glycoside with the 5-position of the aglycone unsubstituted (Evis. max. = 528, Euv. max. = 279 nm, E440 nm/Evis. max. = 25%, E310 nm/Evis. max. = 14%, and +19 nm aluminum chloride shift of Evis. max.). Upon partial acid hydrolysis, three hydrolyzed intermediates having chromatographic mobilities identical to 3-sambubioside, 3-arabinosylglucoside,[1] and 3-glucoside of cyanidin were detected. These hydrolyzed intermediates were found to occur naturally in higher amounts in the two cultivars of *V. trilobum* L. examined.[2] Complete acid hydrolysis yielded cyanidin as the aglycone, and approximately equal amounts of xylose, arabinose and glucose as the hydrolyzed sugars. Hydrogen peroxide hydrolysis removed a trisaccharide from the pigment, different from xylosylrutinose and glucosylrutinose (Rg in BAW, 21; BBPW, 30; BFW, 6; reference xylosylrutinose Rg in BAW, 36; BBPW, 58; BFW, 12).

From the above evidence, the pigment was identified as a new cyanidin 3-trioside containing a branched trisaccharide based on glucose, xylose and arabinose. The identity of the hydrolyzed intermediates suggest that the pigment is Cy-3-arabinosylsambubioside.

EXPERIMENTAL

Plant materials. Ripe berries of *Viburnum trilobum* L. were macerated with 1% HCl in MeOH, filtered, conc. *in vacuo*, and purified on Amberlite CG-50 ion exchange resin.[3] The conc. eluate was allowed to evaporate and extracted with ethyl acetate to remove proanthocyanins and other flavonoids. The purified pigment extract was

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further separated and purified by paper chromatography. All chromatograms were developed by downward migration of the solvent. Whatman No. 3 paper sheets were used for preparative work; for all other purposes Whatman No. 1 chromatography paper was employed.

Solvent systems. BFW (*n*-BuOH–HCO_2H–H_2O, 20:5:12, upper phase). BAW (*n*-BuOH–HOAc–H_2O, 4:1:5:, upper phase), BEW (*n*-BuOH–EtOH–H_2O, 4:1:2:2), BBPW (*n*-BuOH–C_6H_6–pyridine–H_2O, 5:1:3:3) 15% HOAc, HOAc–HCl (HOAc–conc HCl–H_2O, 15:3:82), 1% HCl, Formic (HCO_2H–conc HCl–H_2O, 5:2:3), Forestal (HOAc conc HCl–H_2O, 30:3:10), Phenol (PhOH–H_2O, 4:1), MAW (MeOH–HOAc–H_2O, 18:1:1).

Isolation of pigment. The pigment used in this study was obtained by collecting the fastest moving band in 15% HOAc of *V. trilobum* L. The use of 1% HCl or other HCl containing solvents were avoided to minimize the occurrence of arabinose as an artifact. The collected pigment band contained Cy-3-xylosylrutinoside as the major anthocyanin and was rechromatographed in BFW for 5 days after elution with MAW. The pigment band appearing on top of the major Cy-3-xylosylrutinoside was collected, pooled, re-run in BFW and finally in 15% HOAc.

Identification of pigments. The identification of pigment followed in general the chromatographic and spectroscopic procedure described by Harborne.[4] All pigments and hydrolyzed products were compared with authentic markers on the same chromatograms in several solvent systems. For R_f determinations, the MAW eluate of each pigment was evaporated to dryness, redissolved in 0·5% HCl/MeOH and spotted along with authentic anthocyanins (Cy-3-glucoside from raspberry, Cy-3-sambubioside from red currants, Cy-3-arabinosylglucoside from *V. trilobum* L.[2] and Cy from reductive acetylation[5] of commercial quercetin). Reference trioside, xylosylrutinoside, was obtained from Cy-3-xylosylrutinoside of red currants by hydrogen peroxide hydrolysis.

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Phytochemistry, 1974, Vol. 13, pp. 1999 to 2000. Pergamon Press. Printed in England.

TRITERPENE ACIDS OF INDIAN CLOVE BUDS

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(*Received* 29 *December* 1973)

Key Word Index—*Syzgium aromaticum* (L) Merr.; Caryophyllaceae; triterpene; maslinic acid; naphthalene.

Previous work. Isolation of products from the oil of cloves of unspecified origin; the yield of the products are not given.[1–9]

Present work. Clove buds (dry, Indian origin) (*Syzygium aromaticum* (L.) Merr., *Eugenia caryophyllata* Thumb.) on steam distillation gave, from the phenolic fraction, eugenol,[1,4] (*ca* 16%) and from the neutral fraction, carryophyllene[2] (*ca* 1·6%) and naphthalene (*ca* 0·1%). As there is only one reference in the literature regarding the isolation of naphthalene

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