A NEW SOURCE OF "*l*-QUERCITOL" (VIBURNITOL*)†

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Stephania hernandifolia Walp., family Menispermaceae, a slender climber ranging over the coastal districts of eastern Australia, is reputed to be a stock poison(1). It has been examined by Bancroft(2) who isolated a crude alkaloid fraction and by Rennie and Turner(3) who stated that it contained picrotoxin and an alkaloid. In a new investigation of this plant** the presence of picrotoxin could not be demonstrated with certainty but there was readily obtained a crude mixture of alkaloids which has not yet been separated into its constituents. These matters are receiving further attention. However, by concentrating and cooling an alcoholic extract of the leaves a pure crystalline substance was isolated in 0·4 per cent. yield which was identified as "*l*-quercitol", previously obtained by Power and Tutin(4) from *Gymnema sylvestre* Br.

The substance, which analysed for $C_6H_{14}O_6$, contained one molecule of water of crystallization, lost by drying at 118 °C. in a vacuum pistol. It did not react with triphenylmethyl chloride but a penta-acetyl and a pentabenzoyl derivative were obtained by the usual methods. The constants of the substance

* After this work had been completed and submitted for publication it was announced by Posternak and Schopfer (*Helv. Chim. Acta* **33**: 343 (1950)) that "*l*-quercitol" and viburnitol are identical and that the substance is 2,3,5/4,6-*cyclo*hexane-pentol. These authors have decided to retain the name viburnitol.

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and its two derivatives found in the present work are compared in Table 1 with those reported by Power and Tutin(4). The agreement between some of the figures is excellent but the wide discrepancies in others at first rendered the identification doubtful.

TABLE 1

Present Work	Power and Tutin
" *l*-Quercitol "	
m.p. 181·5 °C.	m.p. 174 °C.
$[\alpha]_D^{20°}$ —50·0° (*c*, 4%) in water	$[\alpha]_D$ —73·9° (*c*, 4·035%) in water
Penta-acetyl " *l*-quercitol "	
m.p. 125·5 °C. (*a*)	m.p. 124–5 °C.
$[\alpha]_D^{20°}$ —22·0° (*c*, 2%) in chloroform	$[\alpha]_D$ —26·0 (*c*, 2·697%) in chloroform
Pentabenzoyl " *l*-quercitol "	
m.p. 158·5 °C.	m.p. 133 °C. (*b*) 148 °C. (*c*)
$[\alpha]_D^{20°}$ —79·0° (*c*, 2%) in chloroform	$[\alpha]_D$ —79·0° (*c*, 2·826%) in chloroform

(*a*) The benzene solvated form, m.p. 87–97 °C., could not be obtained. (*b*) Amorphous, purified from alcohol. (*c*) Obtained by adding light petroleum to an alcohol-ethyl acetate solution and then drying at 100 °C. This form could not be prepared.

Fortunately however, a small amount of Power and Tutin's original specimen of " *l*-quercitol " was made available to us for comparison. On re-examination it was found to have m.p. 181·5 °C., $[\alpha]_D^{20°}$ —50·0° (*c*, 1%) in water and its penta-acetyl derivative, m.p. 125·5 °C., $[\alpha]_D^{20°}$ —21·0° (*c*, 1%) in chloroform. In addition no depressions were observed on taking mixed m.p. of the two substances and of their acetyl derivatives. It must be concluded that the two substances are identical and that the constants given by Power and Tutin are erroneous.

Experimental

Isolation of " l-*Quercitol* ".—The dried and ground leaves and twigs were exhausted with alcohol at room temperature and the extract concentrated under reduced pressure to a fairly thick syrup. After standing in the refrigerator for several days the " *l*-quercitol " crystallized out. It was collected, washed thoroughly with ether, and recrystallized from alcohol, forming colourless needles, m.p. 181·5 °C. after sintering at about 110 °C. Found: C, 39·2; H, 7·9%. Calculated for $C_6H_{14}O_6$: C, 39·5; H, 7·8%. Found: loss of weight on drying at 118 °C. *in vacuo* 9·8%. Calculated for $C_6H_{12}O_5.H_2O$: 9·9%. Found in anhydrous material: C, 43·7; H, 7·5%. Calculated for $C_6H_{12}O_5$: C, 43·9; H, 7·4%.

Penta-acetyl " l-*Quercitol* ".—A solution of " *l*-quercitol " (0·5 g.) in pure dry pyridine (8 ml.) containing excess acetic anhydride (6 g.) was refluxed for 1 hour and then poured into water. The product (90% yield) which separated on standing, crystallized from water in colourless needles, m.p. 125·5 °C. (Found: C, 51·3; H, 5·8%. Calculated for $C_{16}H_{22}O_{10}$: C, 51·3; H, 5·9%.)

Pentabenzoyl " l-*Quercitol* ".—A solution of " *l*-quercitol " (0·5 g.) and excess benzoyl chloride (3·5 g.) in pure dry pyridine (8 ml.) was refluxed for 1 hour and then diluted with water.

The separated oil gradually solidified. The product (80% yield) was collected, washed thoroughly with water, and recrystallized from alcohol from which it separated as colourless needles, m.p. 158·5 °C. (Found: C, 71·8; H, 4·6%. Calculated for $C_{41}H_{32}O_{10}$: C, 71·9; H, 4·7%.)

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References

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