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SHORT COMMUNICATION

CONSTITUENTS OF *SYZYGIUM CORDATUM*

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Abstract—Friedelin, epi-friedelinol, β-sitosterol, arjunolic acid, gallic acid, ellagic acid (hexahydroxydiphenic acid), glucose and a gallic acid–ellagic acid complex were isolated from wood and bark of *Syzygium cordatum*. Leucodelphinidin and leucocyanidin were detected in bark and leaf.

Plant. Syzygium cordatum Hoechst.—Myrtaceae.

Source. A. Port Edward, Natal South Coast, South Africa. *B.* Hlabisa district, Zululand, South Africa.

Identification. A. NH51966 Natal Herbarium, Durban. *B.* NH53048 Natal Herbarium, Durban.

Chemical identity. Samples of the two plants collected from different areas of Natal and growing under different conditions could not be distinguished chemically.

Previous work. Sister species *S. cuminii.*[1]

Bark. Among the sixteen constituents shown to be present in the hexane extract the major components were isolated and identified as friedelin, epi-friedelinol and β-sitosterol. The same compounds were identified in the ether extract together with arjunolic acid. Gallic and ellagic acids were identified in the acetone extract. Prolonged hot mineral-acid treatment of fresh and dried bark gave rise to delphinidin as the only anthocyanidin, probably derived from leucodelphinidin or related polymers.

Sapwood. All constituents present in the hexane extract of the bark were identified in a similar extract of the sapwood, but with reduced concentrations of friedelin and epi-friedelinol and an increased concentration of β-sitosterol. Arjunolic acid* was isolated as the major constituent from the ether extract. Gallic acid, ellagic acid, glucose and a complex yielding gallic and ellagic acids in a 1:3 ratio on hydrolysis, were isolated from the acetone extract, while hexahydroxydiphenic acid was identified chromatographically. The presence of tannin was indicated by its removal from an aqueous solution with polyamide.[2]

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* The i.r. spectrum and chromatographic characteristics of a sample of "tomentosic acid" kindly supplied by Dr. W. P. Schneider were identical to those obtained for arjunolic acid. Since the identity of the "tomentosic acid" isolated by Schneider *et al.* from *Bixa orellana*[3] was dependent upon direct comparison with the "tomentosic acid" isolated from *Terminalia tomentosa*[4,5] it would appear that this acid as such does not exist and is in fact arjunolic acid.

[1] P. Sengupta and P. B. Das, *J. Indian Chem. Soc.* **42**, 255 (1965).

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[3] W. P. Schneider, E. D. Caron and J. W. Hinman, *J. Org. Chem.* **30**, 2856 (1965).

[4] L. Ramachandra Row and G. S. R. Subba Rao, *Tetrahedron Letters* 12 (1960).

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Heartwood. The hexane and ether extracts were chemically similar to those of the sapwood. Gallic and ellagic acids were the major constituents of the acetone extract but glucose and the gallic–ellagic acid complex were absent.

Leaves. The two anthocyanidins obtained after prolonged hot acid hydrolysis of fresh leaves were delphinidin and cyanidin as the major and minor components respectively. The presence of leucoanthocyanidins was indicated by a positive vanillin reaction.[6]

EXPERIMENTAL

Friedelin $C_{30}H_{50}O$. Found: m.p. 264–265°; $[\alpha]_D^{25}$ $-26°$, $CHCl_3$; C, 84·1; H, 12·0; oxime, m.p. 291–292°; i.r. identical to that for authentic friedelin; co-chromatography. Required: m.p. 262–263°; $[\alpha]$ $-29°$; C, 84·4; H, 11·8; oxime, m.p. 290–294°.[7]

epi-Friedelinol $C_{30}H_{52}O$. Found: m.p. 283–284°; $[\alpha]_D^{25}$ $+16°$, $CHCl_3$; acetate, m.p. 290–292°; i.r. identical to that obtained for authentic epi-friedelinol; co-chromatography. Required: m.p. 278–280°; $[\alpha]$ $+15°$, $CHCl_3$; acetate, m.p. 290–294°.[7]

β-Sitosterol $C_{29}H_{40}O.MeOH$. Found: m.p. 136–137°; $[\alpha]_D^{25}$ $-32°$, $CHCl_3$; C, 83·6; H, 12·2; acetate, m.p. 124–126°; benzoate, m.p. 145°; i.r. identical to that obtained for authentic β-sitosterol; co-chromatography. Required: m.p. 136–137°; $[\alpha]$ $-35°$, $CHCl_3$; C, 83·7; H, 12·2; acetate, m.p. 134°; benzoate, m.p. 145·5°.[7]

Arjunolic acid $C_{30}H_{48}O_5$. Found: m.p. 338–339°; $[\alpha]_D^{25}$ $+63°$, EtOH; methyl ester, m.p. 214–215°, M^+ 502; arjunolic acid triacetate, m.p. 179–183°, M^+ 614; methyl arjunolate triacetate, M^+ 628;* the m.s. of methyl arjunolate was almost identical to that given by its 2β-epimer methyl bayogenate. Required: m.p 337–340°; $[\alpha]$ $+63·5$, EtOH;[7] methyl ester, m.p. 215–216°,[8] M^+ 502; arjunolic acid triacetate, M^+ 614; methyl arjunolate triacetate, M^+ 628.

Gallic acid. The i.r. was identical to that of authentic gallic acid; co-chromatography.

Ellagic acid. Found: m.p. >360° dec.; tetraacetate, m.p. 337–340°; ellagorubin, m.p. 214–215°; i.r. of the tetraacetate was identical to that obtained for the authentic tetraacetate; co-chromatography; λ_{max}^{EtOH} 366 and 255 nm; $\lambda_{max}^{EtOH+NaOAc}$ 355, 277 and 255 nm. Required: m.p. >360 dec.; tetraacetate, m.p. 343–346°; ellagorubin, m.p. 214–215°[7] λ_{max}^{EtOH} 366 and 255 nm; $\lambda_{max}^{EtOH+NaOAc}$ 355, 277 and 255 nm.[10]

Hexahydroxydiphenic acid. Two-dimensional chromatography on Whatman No. 1 paper; butanol–HOAc–water (4:1:12), R_f 0·1; 6% HOAc–2% HCO_2H, R_f 0·7; co-chromatography.

Gallic–ellagic acid complex. M.p. 230–240°. Two-dimensional chromatography on Whatman No. 1 paper; butanol–HOAc–water (4:1:12), R_f 0·18; 6% HOAc–2% HCO_2H, R_f 0·28. Hydrolysis: The complex (6 g) refluxed with 5% H_2SO_4 for 22 hr yielded ellagic acid (4·4 g) and gallic acid (1·4 g) only.

α-D-Glucose. Found: m.p. 146–147°; i.r. identical to that obtained for authentic α-D-glucose; co-chromatography; osazone, m.p. 211–213°. Required: m.p. 146–150°; osazone, m.p. 210°.[7]

Anthocyanidins. The anthocyanidins were extracted from the fresh leaves and bark by the usual methods[6, 11] and separated by chromatography on Whatman No. 1 paper using the Forestal solvent. The anthocyanidin bands were eluted with 95% EtOH for spectral measurements.

Delphinidin. Co-chromatography. Found: $\lambda_{max}^{EtOH-HCl}$, 554 nm; $\Delta\lambda^{AlCl_3}$, +27 nm. Required: $\lambda_{max}^{EtOH-HCl}$, 557 nm; $\Delta\lambda^{AlCl_3}$, +23 nm.[12]

Cyanidin. Co-chromatography. Found: $\lambda_{max}^{EtOH-HCl}$, 545 nm; $\Delta\lambda^{AlCl_3}$, +18 nm. Required $\lambda_{max}^{EtOH-HCl}$, 545 nm; $\Delta\lambda^{AlCl_3}$, +18 nm.[12]

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* Due to tenacious retention of solvent no good C and H analysis figures could be obtained.[5, 9]

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