SOME EXTRACTIVES FROM *GEIJERA SALICIFOLIA* SCHOTT.*

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To obtain supplies of the alkaloid, platydesmine, which were required for further study of its conversion into dictamnine,[1] the leaves of *Geijera salicifolia* Schott., the best recorded source of the former alkaloid, were extracted. The results of Johns and Lamberton[2] were duplicated but in addition other fractions of the extract were examined.

The "acidic" fraction yielded umbelliferone but the "phenolic" fraction, which presumably contained zanthoxylin which has been recorded as a constituent of the essential oil,[3] was accidently lost. The "neutral" fraction gave, in addition to β-sitosterol, two other products. The first of these was identifed as the complex coumarin, geiparvarin, whose isolation from the leaves of *G. parviflora* Lindl. and structure determination have been described by Lahey and co-workers.[4,5] The second product, which was beautifully crystalline, melted fairly sharply at 120–121° and with several solvent systems on thin-layer chromatography plates behaved as a single substance. However, gas chromatography demonstrated clearly that it was a mixture of two components, and n.m.r. spectroscopy allowed them to be identified as the coumarins, geijerin and dehydrogeijerin (approximately 1 : 2). Geijerin (m.p. 121°) has been isolated from the bark of *G. salicifolia* by Lahey and Wluka,[6] and dehydrogeijerin (m.p. 130–131°) accompanies geiparvarin in the leaves of *G. parviflora*.[4] Since the chemistry of these substances has been thoroughly explored, no further work was done on the mixture.

Experimental

Melting points are uncorrected. Light petroleum had b.p. 40–60°. I.r. spectra were measured in Nujol mulls and n.m.r. spectra in deuterochlorofom, on a Varian A60 spectrometer; each signal is described in terms of multiplicity, intensity, chemical shift in p.p.m. from tetramethylsilane, assignment, and coupling constant in that order with the use of the following abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet; (b) broad.

Extraction of G. salicifolia *Leaves*

The material used was from the same bulk sample extracted by Johns and Lamberton[2] (Herbarium specimen TGH 10881 A).

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The dried milled leaves (11 kg) were exhausted with methanol at room temperature. The extract was concentrated to a thin syrup and then shaken with water and chloroform. The chloroform layer was concentrated and the alkaloids removed from it by extraction with 3N H_2SO_4 until the extracts gave only a very faint test with Mayer's reagent. The alkaloid fraction was recovered in the usual way and worked up as described;[2] the yields obtained were those recorded.[2]

The residual chloroform solution was washed with water and then extracted successively with 5% $NaHCO_3$, 5% Na_2CO_3, and 5% NaOH; the extracted materials were recovered in the usual manner.

The bicarbonate extract yielded only a very small amount of dark, intractable material which was discarded. The carbonate extract, a dark green semi-solid mass, was triturated with a little benzene and kept overnight. The solid (1·5 g) which separated was collected, washed with benzene, and re-cycled through dilute Na_2CO_3. The recovered product on crystallization from ethyl acetate afforded umbelliferone (1·1 g), m.p. 228–230°, identified by mixed m.p. and comparison of i.r. and n.m.r. spectra with those of an authentic specimen. The "phenolic" fraction was lost by an accident.

The neutral fraction was dissolved in benzene–light petroleum (1000 ml; 1 : 2) and the solution extracted with methanol–water (5 × 200 ml; 9 : 1). The extracts were evaporated to a small bulk and then shaken with ether. The ether was removed and the residue dissolved in methanol (500 ml). On keeping at 0° for several days, crude crystalline geiparvarin (3·3 g), m.p. 153–156°, separated. Recrystallization from methanol and ethanol gave nearly colourless prisms of geiparvarin, m.p. 159–160° (lit.[4] 160–161°), which was identified from the published i.r.[4] and n.m.r. spectra.[5] The combined methanol filtrates were evaporated and the residue chromatographed on alumina deactivated by ethyl acetate. The benzene–light petroleum and the first benzene eluates contained the geijerin–dehydrogeijerin mixture, intermediate eluates contained all three coumarins, and the ethyl acetate–benzene (1 : 99) eluates yielded geiparvarin. By recrystallization and by re-chromatographing the appropriate combinations of fractions and mother liquors, there was eventually isolated additional geiparvarin (2·5 g) and the geijerin–dehydrogeijerin mixture (2·0 g). The mixture crystallized from ethanol as prisms, m.p. 120–121°; ν_{max} 1740, 1670, 1620 cm^{-1}; n.m.r. spectrum (dehydrogeijerin) ABq, 1+1, 7·61 and 6·25, C4–H and C3–H, *J* 9·2; s, 1, 7·2, C5–H; s (b), 1, 6·82, C8–H; m, 1, 6·6, C=CH–CO; s, 3, 3·94, OCH_3; 2 × s (b), 2·24, 1·98, $(CH_3)_2$ C=C; (geijerin) s, 1, 7·8, C5–H; ABq, 1+1; 7·61 and 6·25, C4–H and C3–H, *J* 9·2; s (b) 1, 6·82, C8–H; s, 3, 3·98, OCH_3; d, 1, 2·82, CH_2; m, 1, under CH_3 signals around 2, CH; d, 6, 1·96, $(CH_3)_2CH$. The proportions were estimated by a consideration of the intensity of the signals at 6·6, 2·82, and 1·96.

Material remaining in the benzene–light petroleum layer was saponified and the neutral fraction recovered. Chromatography on alumina yielded only β-sitosterol (0·7 g), m.p. 135–137°, identified by comparison (mixed m.p. and i.r. spectra) with an authentic specimen.

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