A NEW AMIDE FROM *EVODIA HUPEHENSIS* FRUIT HULL[1]

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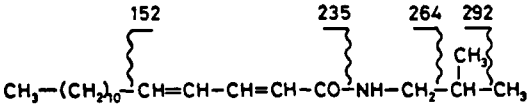
Previous chemical investigation of *Evodia hupehensis*, syn. *Tetradium danielli* (1), led to the characterization of coumarins, alkaloids, terpenes, and other metabolites (2, 3). Further work on the fruit hull has led to the isolation and identification of a new amide (2*E*, 4*E*)-*N*-isobutylhexadeca-2,4-dienamide (**1**), and three known components: (2*E*, 4*E*)-*N*-isobutyldeca-2,4-dienamide (**2**), and 8-isopentenylnaringenin and its 7-*O*-glucoside (flavaprine).

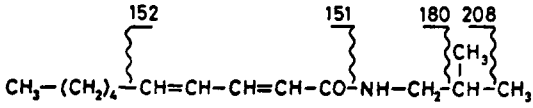
EXPERIMENTAL

PLANT MATERIAL—The plant material was collected from a tree growing in the Medicinal Plants Garden of the Institute of Pharmaceutical Biology and Phytochemistry, Münster.

EXTRACTION AND ISOLATION—Air-dried fruit hulls (235 g) were extracted for 7 days with EtOH. Concentration of the EtOH extracts to a small volume in vacuo afforded a precipitate (262 mg) which was isolated by filtration. The filtrate was evaporated to dryness, taken up in $MeOH/H_2O$ (2:1, v/v) and shaken with toluene (3 × 100 ml). The toluene extract was concentrated to a small volume to yield a precipitate (146 mg, 0.5%, mp 81-86°), identified as (2*E*, 4*E*)-*N*-isobutyl-2,4-decadienamide (**2**) (mp, ir, ^1H nmr, uv, and ^{13}C nmr).



1 (*m/z*, 307)



2 (*m/z*, 223)

The toluene-soluble fraction was chromatographed over silica gel and eluted with toluene/EtOAc mixtures to afford (2*E*, 4*E*)-*N*-isobutylhexadeca-2,4-dienamide (**1**) (6 mg, 0.020%) as a non-crystallizable, sticky, yellow compound. Compound **1** was characterized by the following spectral data uv, λ max 257 nm (+NaOH) no shift; ir, ν max KBr 3320, 3090, 2965, 2938, 2862, 1660, 1645, 1620, 1465, 1380, 1275, 998 cm^{-1}; ^1H nmr, δ ($CDCl_3$) 0.85 (3H,t,J,=7 Hz, Me), 0.92 (6H,d,J,=6.8 Hz, CMe_2), 1.26 (16H, m, $8CH_2$), 141 (2H, m, CH_2), 2.04 (1H, m, $CHMe_2$), 2.21 (2H, m, CH_2), 3.17 (2H, t, J=6.5 Hz, N-CH_2), 5.52 (1H, m, NH), 5.77 (1H, d, J=15 Hz, α-CH), 6,08 (2H, m, γ- and δ-CH), 7.32 and 7.45 (1H, AB q, J=9.8 Hz, β-CH; and ms *m/z* (rel. int.) 307 $[M]^+$ (10), 292$[M-CH_3]^+$ (4), 279 $[M-C_2H_4]^+$ (15), 264 $[M-CHMe_2]^+$ (22), 236 $[M-CH_2CHMe_2]^+$ (18), 207 $[M-CONCH_2CHCMe_2]^+$ (95), 167, 152, 151, 149, 121, 110, 96, 81. The ^1H nmr of (**1**) showed the same signals as (**2**) with an extra signal which integrated for 16 protons and representing an additional 4 methylenes at δ 1.26. 8- Isopentenylnaringenin (23 mg, 0.078%) and 8-isopentenylnaringenin-7-*O*-glucoside (flavaprine) (52 mg, 0.18%) were identified by their mp, ir, ^1H nmr, uv, and ms (4,5).

Full details of the isolation method and analytical data for the known chemicals are available on request to the senior author.

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AURANTIAMIDE ACETATE, QUASSINOIDS, AND A CANTHINONE FROM THE STEM BARK OF *PIERREODENDRON KERSTINGII*

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Pierreodendron kerstingii (Engl.) Little (Simaroubaceae) is a large tree from the rain forest of west tropical Africa (1). In a previous investigation of the stem bark, Kupchan and Lacadie (2) reported four typical simaroubaceous quassinoids; ailanthinone, 2′-acetylglaucarubinone, glaucarubinone, and dehydroailanthinone.

We have recently reinvestigated the stem bark and, in addition to ailanthinone, glaucarubinone, and 2′-acetylglaucarubinone, have isolated three further quassinoids, excelsin, 2′-acetylglaucarubin and, as the major compound, glaucarubin. Of the quassinoids new from this species, the first two were confirmed by direct comparison with material recently isolated from *Odyendyea gabonensis* Engl. (3) while glaucarubin was identified by comparison of ^{1}H- and ^{13}C-nmr spectra with other closely allied quassinoids (3) and with literature data (4, 5). Nonquassinoid compounds isolated were 8-hydroxycanthinone, also previously reported from *O. gabonensis* (3), and aurantiamide acetate (asperglaucide). The latter, which is an unusual amide based on phenylalanine and phenylalaninol units with benzoyl and acetyl substituents, was identified by comparison of spectral data with those published (6-8). Aurantiamide acetate has previously been isolated from several sources, including the fungus *Aspergillus glaucus* (6), the alga *Cytoseira corciculata* (7), and *Piper aurantiacum* (8). A microscopic examination of the bark sample failed to reveal any sign of mycelia, thereby ruling out the possibility that aurantiamide acetate was present due to fungal contamination of the bark during drying.

EXPERIMENTAL

PLANT MATERIAL.—*P. kerstingii* stem bark was collected from riverine forest in Ghana in 1982. A voucher, FE-2147, has been deposited at the Herbarium of the Royal Botanic Garden, Edinburgh.

EXTRACTION AND ISOLATION.—Powdered stem bark (600 g) was extracted successively with petroleum ether (60-80°), $CHCl_3$, and MeOH. Column chromatography of the petroleum ether extract over silica gel gave, on elution with petroleum ether containing 10% EtOAc, β-sitosterol (20 mg). Further elution with 35% EtOAc gave aurantiamide acetate (110 mg). Similar treatment of the concentrated $CHCl_3$ extract, eluting with $CHCl_3$ containing increasing amounts of MeOH gave: (a) with 1% MeOH, a mixture of ailanthinone and 2′-acetylglaucarubinone followed by 8-hydroxycanthin-6-one (55 mg), (b) with 3% MeOH, glaucarubinone (70 mg), (c) with 5% MeOH, a mixture of excelsin and 2′-acetylglaucarubin, and (d) with 10% MeOH, glaucarubin (250 mg). The two mixtures were separated by circular preparative tlc on silica gel. Using CH_2Cl_2-iPrOH (49:1) as solvent gave ailanthinone (25 mg) and 2′-acetylglaucarubinone (12 mg); CH_2Cl_2-iPrOH-HOAc (95:5:0.5) gave excelsin (22 mg) and 2′-acetylglaucarubin (9 mg).