

Present work. The fractions with polarity of 4,4-dimethylsterols and 4-monomethylsterols were isolated from non-saponifiable lipids of 10-day-old *Cucumis sativus* cv. Wisconsin seedlings by Al_2O_3 column chromatography and subsequent TLC purification. Both fractions were acetylated and their components separated by AgNO_3 -silica gel TLC. Pure cycloartenol acetate, 24-methylenecycloartenol acetate and 24-ethylidenelophenol acetate (4.1, 2.0 and 2.3 mg/100 g of dry plant material respectively) were obtained and characterized by m.p., TLC, GLC (SE-30 and OV-17) and MS [6,7]. Cycloeucalenol acetate, 24-methylenelophenol acetate and obtusifolioside acetate (3.6, 0.9 and 0.4 mg/100 g of dry plants) were isolated as not quite homogeneous fractions and identified by TLC, GLC and MS of whole fractions. Only two minor components (less than 5% of sterol precursor fraction) could not be identified. Therefore, we were able to identify in *C. sativus* only typical

sterol precursors isolated previously from a number of higher plants [4,6,7]. Additionally a mixture of pentacyclic triterpenic monoalcohols; β - and α -amyrin (20.5 and 1.5 mg per 100 g of dry plants respectively) was isolated and characterized by TLC, GLC and MS. We were unable to prove the occurrence of parkeol in *C. sativus*.

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THE IDENTIFICATION OF ACETYLRAMOSIN C AS TETRA-ACETYLSWERTIAMAROSIDE

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One of us reported [1] the isolation of three glycosides, acetylramosins A, B and C, from the Pakistan medicinal plant *Erythraea ramosissima* Pers. (Gentianaceae). We wish now to present evidence which shows that acetylramosin C is identical with tetra-acetylswertiamaroside.

Acetylramosin C, m.p. 191° , $[\alpha]_D - 110^\circ$ (c, 0.4; CHCl_3) analysed for $\text{C}_{24}\text{H}_{30-32}\text{O}_{14}$ [1]. Its IR spectrum showed strong absorptions at 1750 and 1220 cm^{-1} (acetoxy groups), 1705 and 1625 cm^{-1} (α , β -unsaturated δ -lactone), and 905 cm^{-1} (vinyl group); and its UV spectrum exhibited a λ_{max} 236 nm (ϵ 8750), characteristic of an α , β -unsaturated δ -lactone moiety [2]. Strong ions in the MS at m/e

331, 271, 211, 169 (base peak), 127 and 109 indicated the presence of a tetra-acetoxyglucosyl moiety, and an ion at m/e 195 showed that acetylramosin C had a molecular formula $\text{C}_{24}\text{H}_{30}\text{O}_{14}$. The loss of 18 amu from the ion m/e 195 showed that it contained a hydroxyl group on the terpenoid moiety.

The NMR spectrum revealed the presence of four acetoxy groups (δ 2.01-2.10); an olefinic proton on a carbon atom bearing oxygen (δ 2.55; 1H, s; H_3); an allylic proton (δ 2.92; 1H, m; H_9) which collapsed to singlet on irradiation at δ 5.33; a proton on a carbon atom bearing two oxygen atoms (δ 5.46; 1H, d, J 1.5 Hz; H_1) which collapsed to a

singlet on irradiation at δ 2.92; methylene protons (δ 1.78; 2H, *m*; C₆) which collapsed to a broad singlet on irradiation at δ 4.82; methylene protons at δ 4.47 (1H, *m*; H₇) and δ 4.92 (1H, *m*; H₇) which collapsed to an *AB* quartet ($J \approx 5.00$ Hz) an irradiation at δ 1.78; and a tertiary hydroxyl group (δ 3.75; 1H, *s*).

The above spectroscopic data suggested that acetylramosin C was tetra-acetylswertiamaroside [2]. This was confirmed by direct comparison of the IR and NMR spectra of the two compounds and a mixed m.p. determination.

EXPERIMENTAL

The IR spectrum was measured as a KBr disc, the UV spectrum in EtOH, and the NMR spectrum in CDCl₃. The MS was recorded on a Hitachi Perkin Elmer RMU 6 single focussing spectrometer, and the optical rotation on a Perkin Elmer 141 MC polarimeter.

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XANTHONES FROM THE HEARTWOOD OF CALOPHYLLUM RAMIFLORUM*

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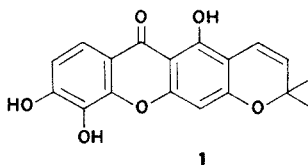
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Key Word Index—*Calophyllum ramiflorum*; Guttiferae; xanthones; jacareubin; 2-(3-methylbut-2-enyl)-1-hydroxy-3,5,6-trimethoxyxanthone; euxanthone; 1,7-dihydroxyxanthone; 1-hydroxy-6,7-dimethoxyxanthone; chemotaxonomy.

Plant. *Calophyllum ramiflorum* Schwarz, Guttiferae. *Source.* W. Australia, identified by N. Byrnes, Botanist, Primary Industries Branch, Northern Territory Administration, Darwin, and confirmed by the Royal Botanic Gardens and National Herbarium of South Yarra, S.E.1, Victoria. *Previous work.* None on this species, but previous studies on the pigments from Guttiferae heartwoods [1,2] identify largely xanthones, biflavonoids [3] and coumarins [4]. *Calophyllum* species, apart from the Indian variety [5], contain jacareubin (1).



Present work. It has previously been suggested [2,6] that the presence of jacareubin (1) and/or the putative isoprenyl precursor 2-(3-methyl-2-butenyl)-1,3,5,6-tetrahydroxyxanthone (2) may be

of taxonomic value in identifying *Calophyllum* species. Only in the Indian variety of *C. inophyllum* L. are these metabolites absent [5]. Further *Calophyllum* species are under examination for the presence of jacareubin (1) since this metabolite is required as a synthetic relay in the preparation of morellin analogues [7].

Extraction of the powdered heartwood of *Calophyllum ramiflorum* Schwartz with hot CHCl₃ and concentration of the extract gave a solid which contained largely jacareubin. Removal of the solvent from the filtrate gave a mixture which was washed with light petroleum to remove sitosterol, oils and waxes and the residue then chromatographed on silica. Elution CHCl₃–EtOAc led to isolation of 1,7-dihydroxyxanthone (euxanthone) and jacareubin (1) and a mixture of xanthones which were separated by methylation and further chromatography. Jacareubin dimethyl ether, 2-(3-methylbut-2-enyl)-1-hydroxy-3,5,6-trimethoxyxanthone and 1-hydroxy-6,7-dimethoxy-xanthone were identified by isolation and comparison with authentic specimens.

* Part XXVII in the series "Extractives from Guttiferae". For Part XXVI see Ref. 1.