with $CHCl_3$ and 1 l., 24 hr × 2 with 85% aqueous MeOH. The $CHCl_3$ extracts contained no flavonoids and were discarded. The aqueous MeOH extracts were concentrated to 200 ml; this solution was extracted in each case with EtOAc, 500 ml × 5. The EtOAc extracts were evaporated to dryness. For each extract the residue was dissolved in MeOH, and the soln was applied as narrow bands on paper (Whatman 3 MM). The chromatograms were developed one-dimensionally in 15% HOAc for 5 hr. The lowermost band was cut from the paper and eluted 2 × 24 hr with MeOH. The eluate was concentrated and applied to a small column (i.d. 2·5 cm) packed with 10 g of polyamide (Polyclar AT). Elution was accomplished with $CHCl_3$–MeOH (2:1). The concentrate from *N. linearifolia* gave two well separated bands, detected by UV light (366 nm) during the column chromatography; the first band gave **2** (30 mg) while the second gave **1** (20 mg). The concentrate from *N. gracilis* yielded only **3** (8 mg).

Sugar identification utilized a stainless steel column 3 m × 3 mm (i.d.) packed with 80–100 mesh 3% SE 30 on chromosorb G installed in a Varian 600 D gas chromatograph having a flow rate of 25 ml of He/min (measured at the detector end of the column) and an isothermal oven temperature of 180°. The disaccharide released after H_2O_2 oxidation was co-chromatographed with authentic neohesperidose (prepared from natural naringenin 7-*O*-neohesperidoside) in four solvents; co-electrophoresis of the sugars was accomplished on paper in borate buffer pH 10 at 15 V/cm for 6 hr. All sugars were identical with neohesperidose. All other procedures were those as outlined in Mabry *et al.* [3].

Quercetin 3-O-*neohesperidoside* **1**. Color test: purple (UV) to yellow-brown (UV/NH_3); R_fs: TBA 0·54, HOAc 0·78, UV, λ_{max} (nm): MeOH, 354, 296sh, 266sh, 255; NaOMe, 401, 325 272; $AlCl_3$, 436, 302sh, 275; $AlCl_3$ HCl, 401, 360, 296sh, 270; NaOAc, 386, 322, 272; NaOAc–H_3BO_3, 374, 308sh, 259. NMR* (CCl_4) 0·83 (*d*, *J* 6·0, 3 H, rhamnosyl Me), 3·65 (*c*, 10 H, sugar protons), 4·81 (1 H, rhamnosyl H-1), 5·75 (1 H, glucosyl H-1), 6·25 (*d*, *J* 2·5, 1 H, H_6), 6·42 (*d*, *J* 2·5, 1 H, H_8), 6·83 (*d*, *J* 8·5, 1 H, H_5), 7·72 (*d*, *J* 8·5, 2 H, H_3 and H_6).

Kaempferol 3-O-*neohesperidoside* **2**. Color test: purple (UV) to green-brown (UV/NH_3); R_fs: TBA 0·70, HOAc, 0·79; UV λ_{max} (nm): MeOH, 348, 298sh, 265; NaOME, 394, 324, 274; $AlCl_3$, 398, 351, 304, 274; $AlCl_3$–HCl, 397, 344, 301, 275; NaOAc, 380, 306, 273; NaOAc–H_3BO_3, 350, 315sh, 266. NMR* (CCl_4): 0·85 (*d*, *J* 6·0, 3 H, rhamnosyl CH_3), 3·65 (*c*, 10 H, sugar protons), 4·83 (1 H, rhamnosyl H-1), 5·75 (1 H, glucosyl H-1), 6·12 (*d*, *J* 2·5, 1 H, H_6), 6·45 (*d*, *J* 2·5, 1 H, H_8), 6·85 (*d*, *J* 9, 2 H, H_3 and H_5), 8·10 (*d*, *J* 9, 2 H, H_2 and H_6).

Isorhamnetin 3-O-*neohesperidoside* **3**. Color test: purple (UV) to yellow-brown (UV/NH_3); R_fs: TBA 0·57, HOAc 0·81, UV λ_{max} (nm): MeOH, 350, 300sh, 268sh, 252; NaOMe, 406, 326, 273; $AlCl_3$, 403, 365sh, 303, 270; $AlCl_3$ HCl, 400, 356, 302, 270; NaOAc, 376, 318, 274; NaOAc–H_3BO_3, 353, 302sh, 263sh, 252.

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* Values are given in ppm (δ scale) relative to TMS as internal standard; spectra were recorded for trimethylsilyl ethers.

REFERENCES

1. Williams, C. A., Harborne, J. B. and Clifford, H. T. (1971) *Phytochemistry* **10**, 1059.
2. Vancraenenbroeck, R., Callewaert, W., Gorissen, H. and Lontie, R. (1969) Europ. Brew. Conv., *Proc. 12th Congr. Interlaken*, p. 29, Elsevier, Amsterdam.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, Springer, Heidelberg.

Phytochemistry, 1975, Vol. 14, pp. 296–297. Pergamon Press. Printed in England.

PENTACYCLIC TRITERPENES AND TYPICAL STEROL PRECURSORS IN *CUCUMIS SATIVUS* SEEDLINGS

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Key Word Index—*Cucumis sativus*; Cucurbitaceae; 4-monomethylsterols; 4,4-dimethylsterols; β- and α-amyrin.

Previous work on triterpenoids. 4-desmethylsterols (mainly stigmasta-7,22,25-trien-3β-ol and stigmasta-7,25-dien-3β-ol) in seeds [1] and seedlings [2]; cucurbitacins B and C in seedlings [3]. We decided to examine the fraction of sterol precursors of *C. sativus*, since it had been suggested that a different sequence of intermediates may be involved in the biosynthesis of Δ^{25}-sterols than for typical phytosterols such as sitosterol or stigmasterol [4]. A possible role of parkeol (an isomer of cycloartenol) as a biogenetic precursor of cucurbitacins had been considered [5].

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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-methylenecycloartanol 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 obtusifoliol 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*.

REFERENCES

1. Sucrow, W. and Reimerdes, A. (1968) *Z. Naturforsch.* **23b,** 42.
2. Kintia, P. K. and Wojciechowski, Z. A. (1974) *Phytochemistry* In press.
3. Enslin, P. R. (1954) *J. Sci. Food Agr.* **5,** 410.
4. Goad, L. J. (1972) *The Biosynthesis of Plant Sterols in Progress in Phytochemistry* (Reinhold, L. and Liwschitz, Y., eds.), 3, p. 113, Interscience, London.
5. Zander, J. M. and Wigfield, D. C. (1970) *Chem. Commun.* 1599.
6. Nagasampagi, B. A., Rowe, J. W., Simpson, R. and Goad, L. J. (1971) *Phytochemistry* **10,** 1101.
7. Evans, F. J. (1973) *J. Pharm. Pharmac.* **25,** 156.

Phytochemistry, 1975, Vol. 14, pp. 297–298. Pergamon Press. Printed in England.

THE IDENTIFICATION OF ACETYLRAMOSIN C AS TETRA-ACETYLSWERTIAMAROSIDE

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Key Word Index—*Erythraea ramosissima*; Gentianaceae; Acetylramosin C; Tetra-acetylswertiamaroside.

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° (*c*, 0·4; $CHCl_3$) analysed for C_{24} H_{30-32} 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 C_{24} H_{30} 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