Phytochemistry, 1976, Vol. 15, p. 829. Pergamon Press. Printed in England.

NAPHTHAQUINONES AND TRITERPENOIDS OF *EUCLEA DIVINORUM*

M. ÁUREA CRUZ COSTA, M. HELENA LOPES, M. ISABEL PAUL, MARGARIDA A. FERREIRA and A. CORREIA ALVES
Laboratory of Pharmacognosy, Faculty of Pharmacy, University of Oporto, Portugal

(*Received* 29 *December* 1975)

Key Word Index—*Euclea divinorum*; Ebenaceae; naphthaquinones; triterpenoids; diosindigo A; 2-methylnaphthazarin; 7-methyl-juglone; diospyrin; lupeol; betulin.

Plant. Euclea divinorum Hiern was collected 38 km from Lourenço Marques, Mozambique, on the route to Namaacha. Voucher specimens are deposited in the Herbarium of the Laboratory of Botany, University of Lourenço Marques. *Plant material examined. Roots. Previous work.* A sample of the plant, from South Africa, shown to contain 7-methyljuglone, mamegakinone, diospyrin and isodiospyrin in the roots but the stems and fruits contained no quinones [1].

Present work. Dried powdered roots of *E. divinorum* were extracted (Soxhlet) with petrol (bp 50–70°). The extract was concentrated under red pres and submitted to preparative TLC on silica in petrol saturated with MeOH. Three bands were formed, I, II, III, by order of decreasing R_f values. The silica corresponding to each band was removed from the plates and extracted with $CHCl_3$, the chloroform extracts then being rechromatographed under the same conditions. Band I yielded diosindigo A and band II 2-methylnaphthazarin. The $CHCl_3$ extract corresponding to band III was chromatographed on silica in $CHCl_3$, yielding two bands (IIIa, IIIb). Band IIIa yielded 7-methyljuglone and band IIIb diospyrin. All substances were identified by direct comparison with authentic samples (mp, TLC, UV, IR). It is interesting to note that 2-methylnaphthazarin, a somewhat rare substance [2], was found earlier by us in *E. lanceolata* E. Mey ex D C: [3] and in *E. pseudebenus* E. Mey ex DC. [4]. Diosindigo A [5], a common constituent of *Diospyros* spp. [6], has also been isolated from four *Euclea* spp. [1,7].

Another portion of the petrol extract was chromatographed over silicic acid, and the column eluted with solvents of increasing polarity. Petrol–C_6H_6 (8:2) removed triterpenoid compounds. The solvent was evaporated under red pres and residue obtained was chromatographed over alumina. Elution with petrol–C_6H_6 (3:7; 2:8) gave lupeol, $M^+ = 426$, mp 214–215° (MeOH and Me_2CO), $[\alpha]_D^{20} + 27.3°$; acetate, $M^+ = 468$, mp = 212° (Me_2CO), $[\alpha]_D^{20} + 47.1°$ ($CHCl_3$) while C_6H_6–$CHCl_3$ (2:8) and $CHCl_3$ yielded betulin, $M^+ = 442$, mp 258–260° (Me_2CO) $[\alpha]_D^{20} + 19°$ (pyridine); diacetate $M^+ = 526$, mp 219–220° (Me_2CO), $[\alpha]_D^{20} + 21.9$ ($CHCl_3$). The identifications were confirmed in all cases by direct comparison with authentic samples (TLC, IR, NMR).

Acknowledgements—We thank the Laboratory of Botany, University of Lourenço Marques, Mozambique, for the offer of plant material, and Dr. A. Adélia Diniz, from the same Laboratory, for having classified this material. We also thank the "Instituto de Alta Cultura" for financial support (Research Project PFR/7).

REFERENCES

1. Vijver, L. M. V. D. and Gerritsma, K. W. (1974) *Phytochemistry* **13**, 2322.
2. Thomson, R. H. (1971) *Naturally Occurring Quinones*, 2nd Edn, Academic Press, London.
3. Correia Alves, A., Cruz Costa, A. and Ferreira, M. A. (1969) *Garcia de Orta, Lisboa*, **17**, 299.
4. Ferreira, M. A., Cruz Costa, A., Correia Alves, A. and Lopes, M. Helena, (1973) *Phytochemistry* **12**, 433.
5. Musgrave, O. C. and Skoyles, D. (1970) *Chem. Commun.* 1461.
6. Musgrave, O. C. and Skoyles, D. (1974) *J. Chem. Soc. Perkin I*, 1128.
7. Ferreira, M. A., Cruz Costa, M. A., Correia Alves A. and Lopes, M. Helena (1973) *Phytochemistry* **12**, 433.

Phytochemistry, 1976, Vol. 15, pp. 829–830. Pergamon Press. Printed in England.

STEROLS AND TRITERPENES FROM THE FRUIT OF *ARTOCARPUS ALTILIS*

LAWRENCE J. ALTMAN and S. WILLIAM ZITO
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794, U.S.A.

(*Received* 5 *November* 1975)

Key Word Index—*Artocarpus altilis*; Moraceae; breadfruit; sterols; triterpenes; cycloartenol; α-amyrin; cycloart-23-ene-3β,25-diol; cycloart-25-ene-3β,24-diol.

Plant. Artocarpus altilis. Source. Hunts Point Fruit Market, Bronx, New York. *Use.* Foodstuff. *Previous work.* Isolation of cyclopropane sterols from the bark and sister species [1].

Present work. The fresh fruit (1.4 kg) was extracted with $CHCl_3$. The solvent evaporated to give a residue (6.8 g) which was saponified. The non-saponifiable extract (3.3 g) in Et_2O was subjected to preparative layer

TLC on silica gel. Development with CH_2Cl_2 yielded 2 fractions. The first fraction (0.9 g) was acetylated and dry-column chromatographed on 12% $AgNO_3$–impregnated Si gel. Elution with CH_2Cl_2 yielded α-amyrin acetate (0.197 g [2]) identified by direct comparison of IR, NMR, MS, mmp and co-chromatography (TLC and GC) with reference compound. The dry-column also afforded cycloart-24-en-3β-yl acetate (0.375 g [2]) which was identified by direct comparison with cycloartenyl acetate prepared from cycloart-24-en-3-one isolated from *A. integrefolia* (jackfruit) [3]. The second fraction (1.6 g) was repeatedly chromatographed on preparative layer silica gel plates with 1% EtOH: Benzene and yielded two compounds. The first was cycloart-23-ene-3β,25-diol (0.498 gm) [2,3], mp 200–201°. MS: M^+ 442 (0.1%), *m/e* (%), 427 (0.1), 424 (0.9), 409 (2.0), 391 (0.7), 313 (0.6), 302 (1.1), 297 (1.6), IR: ν_{max}^{KBr} 3300 cm^{-1}. NMR: δ0.32 (1 H,*m*), δ0.58 (1 H,*m*), δ1.3 (6 H,*s*). Acetylation of this diol (0.398 g) yielded the expected monoacetate (0.350 gm)[2], mp 149–150°. MS: M^+ 484 (0.3%), *m/e* (%), 469 (0.4), 424 (11.7), 391 (0.9), 313 (0.5), 302 (1.7), 297 (8.2). IR: ν_{max}^{KBr} 3300, 1725 cm^{-1}, NMR: δ0.32 (1 H,*m*), δ0.58 (1 H,*m*), δ2.1 (3 H,*s*). Reduction of the monoacetate (0.125 g) with H_2 over 10% Pd/C yielded cycloartan-3β-yl acetate (0.100 g)[2] which was identical in all respects with reference material. The second compound was cycloart-25-ene-3β,24-diol[4] (0.695 g)[2], mp 186–188°. MS: M^+ 442 (0.1%), *m/e* (%), 427 (0.2), 424 (0.7), 409 (1.1), 391 (0.4), 313 (0.3), 302 (0.8), 297 (0.8). IR: ν_{max}^{KBr} 3300 and 896 cm^{-1}. NMR: δ0.32 (1 H,*m*), δ0.58 (1 H,*m*), lacked the δ1.3 (6 H,*s*) of the 3β,25 diol. Acetylation afforded the expected diacetate (0.6 gm)[2], mp 147–149°. MS: M^+ 526 (0.8%), *m/e* (%), 511 (0.2), 466 (12.5), 409 (1.1), 391 (7.1), 253 (1.1), 302 (1.1), 297 (10.4), IR: ν_{max}^{KBr} 1725 cm^{-1}. NMR: δ0.32 (1 H, *m*), δ0.58 (1 H,*m*), δ2.1 (6 H,*s*). The availability of breadfruit coupled with the relatively substantial amount of cycloartenol (12% of the non-saponifiable extract) make this fruit a valuable source of this cyclopropane containing sterol.

Acknowledgements—One of us (LJA) would like to thank the Alfred P. Sloan Foundation for a fellowship (1971–1975). We also thank Harry Dinerman for technical assistance and the Dominican Republic counsulate for their aid in the purchase of breadfruit out of season.

REFERENCES

1. Pavanasasivam, G. and Sultanbawa, U. S. (1973) *Phytochemistry* **12**, 2725.
2. All yields refer to isolated, recrystallized material (3×).
3. Barton, D. H. R. (1951) *J. Chem. Soc.* 1444.
4. Djerassi, C. and McCrindle, R. (1962) *J. Chem. Soc.* 4034.

Phytochemistry, 1976, Vol 15, pp. 830–831. Pergamon Press. Printed in England.

ISOLATION OF VOMIFOLIOL AND DIHYDROVOMIFOLIOL FROM *CANNABIS**

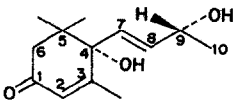
C. A. LUDWIG BERCHT†, HASSAN M. SAMRAH‡, ROBERT J. J. CH. LOUSBERG, HUBERT THEUNS and CORNELIS A. SALEMINK

Organic Chemistry Laboratory, State University Utrecht, The Netherlands

(*Received* 30 *September* 1975)

Key Word Index—*Cannabis sativa*; Cannabinaceae; hemp; vomifoliol; dihydrovomifoliol.

During our research on the non-cannabinoidal nitrogen-containing constituents of Dutch grown hemp, *Cannabis sativa* L. var. Fibrimon-21 (monoecious hemp), we identified the quaternary ammonium bases choline [1] from all parts of the plant, trigonelline [1] and L-(+)-isoleucine betaine [2] from the seeds and trimethylamine [1] from the leaves; in addition evidence was found for the presence of alkaloidal constituents [3]. In a preliminary report [4] we indicated the possible presence of indolic components, because some fractions gave positive reactions on thin-layer plates after development and spraying with Ehrlich's reagent. Now, two of these components have been isolated from both the leaves and the stems of hemp plants. In contrast with the positive reaction with Ehrlich's reagent, the IR and NMR spectra of the two compounds did not give any indication for structures of indolic nature. From these spectra, the isophorone structures **1** and **2** were proposed. **1** is known as vomifoliol [6,7] or blumenol A [8] and **2** is blumenol B [8] or dihydrovomifoliol. The mass spectra of the two compounds were in full agreement with the proposed structures. The measured optical rotation of the compounds was very similar to those published by Weiss *et al.* [9]. Therefore the stereochemistry of the asymmetrical centre is 4S and 9R for both the compounds. Full identity of the two isolated compounds was obtained by synthesis of the racemic structures starting from (+)-α-ionone [10].



(**1**) Vomifoliol
(**2**) Dihydrovomifoliol (single bond at posn. 7–8)

* Part 11 in the series "Cannabis". For Part 10 see C. A. L. Bercht, R. J. J. Ch. Lousberg, F. J. E. M. Küppers and C. A. Salemink, United Nations Secretariat ST/SOA/SER. S/46 (1973).

† Present address: Laboratory of the Ministry of Finance, Amsterdam, The Netherlands.

‡ Present address: Medico Legal Laboratory, 22 El Falaki Street, Cairo, U.A.R.