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.

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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

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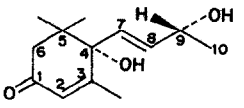
Key Word Index—*Cannabis sativa*; Cannabinaceae; hemp; vomifoliol; dihydrovomifoliol.

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.

EXPERIMENTAL

Isolation. The extraction scheme described by Powell [5] which fractionates indoles was used. Air-dried leaves of Dutch grown *Cannabis sativa* L. var. Fibrimon-21 (19·5 kg) were extracted with in total 160 l. of cold EtOH. After concentration of the extract under red. pres, the remaining residue (2380 g) was extracted with 6 l. CH_2Cl_2. This extract was concentrated and the residue was partitioned between acetonitrile and *n*-hexane. The acetonitrile soluble part was worked up to give an acidic, a basic and a neutral fraction, 2·7, 1·1 and 3·8 g resp. The last two fractions contained the main part of the Ehrlich-positive components and they were combined for further purification. Repeated column chromatography on silica, using $CHCl_3$ containing 1–4% MeOH as the eluent, successively yielded 25 mg of dihydrovomifoliol and 65 mg of vomifoliol (the stems contained 3·2 mg of vomifoliol per kg plant material).

Vomifoliol R_f 0·18 (precoated silica plates "Merck", eluent $CHCl_3$–MeOH (93:7). Gives with Ehrlich's reagent a brownish–red colour, that turns to green. 100 MHz NMR spectrum (in $CDCl_3$): δ1·01(*s*, 3H) 1·08(*s*, 3H), 1·29(*d*, *J* 6·2 Hz, 3H), 1·88(*d*, *J* 1·4 Hz, 3H), 2·00 (broad, 2H), 2·34(H_{AB}, *J* 17 Hz, 2H), 4·39(*m*, *J* 3·5 and 6·2 Hz, 1H), 5·80(*s*, 1H), 5·82(*d*, *J* 3·0 Hz, 1H) and 5·89(*q*, *J* 1·4 Hz, 1H) ppm. IR spectrum: 3400 cm^{-1} (OH) and 1650 cm^{-1} (C = C − C = O). MS spectrum: *m/e* 224(0·5%), 206(3·5%), 168(9·3%),151(3·5%), 150(5·9%), 135(4·5%), 125(10·4%), 124(100%), 123(4·2%), 122(7·1%), 111(6·8%), 107(2·8%), 79(6·3%), 77(4·4%), 69(4·7%).

Dihydrovomifoliol R_f 0·20 (precoated silica plates "Merck", eluent $CHCl_3$–MeOH (93:7). Gives with Ehrlich's reagent a violet colour. 100 MHz NMR spectrum (in $CDCl_3$): δ1·05(*s*, 3H), 1·09(*s*, 3H), 1·21(*d*, *J* 6·0 Hz, 3H), 1·4–2·0(4H), 2·04(*d*, *J* 1·5 Hz, 3H), 2·3(broad, 2H), 2·36(H_{AB}, *J* 18Hz, 2H), 3·75(*m*, *J* 2·0 and 6·0 Hz, 1H) and 5·82(*q*, *J* 1·5 Hz, 1H) ppm. IR spectrum: 3400 cm^{-1} (OH) and 1650 cm^{-1} (C = C − C = O) MS spectrum: *m/e* 226(1·6%), 193(2·4%), 183(4·0%), 171(7·2%), 170(72·6%), 166(6·4%), 154(4·0%), 153(59·7%), 152(77·4%), 151(3·2%), 137(4·0%), 135(3·2%), 127(3·2%), 126(3·2%), 125(25·0%), 124(12·9%), 123(12·0%), 111(63·5%), 110(100%), 109(16·9%), 107(18·5%), 96(33·9%), 95(14·5%), 93(5·6%), 91(8·9%), 83(7·2%), 82(12·9%), 81(6·4%), 79(8·0%), 77(4·0%), 69(20·1%).

Synthetic compounds. Spectroscopic data of the synthetic products were in full agreement with those of the natural products.

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A NEW TRITERPENE GLYCOSIDE FROM *MOLLUGO HIRTA*

A. K. BARUA, S. CHAKRAVARTI, A. BASAK, AMITABHA GHOSH and P. CHAKRABARTI
Department of Chemistry, Bose Institute, Calcutta 9, India

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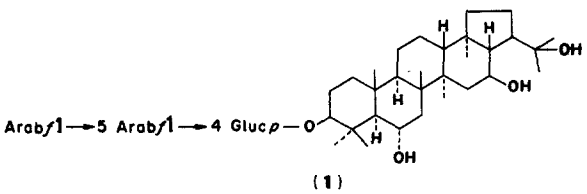
Key Word Index—*Mollugo hirta*; Aizoaceae; triterpene glycoside; mollugocin A.

The isolation of a number of new triterpenoid sapogenins called mollugogenol A, B, C and E[1–5] and oleanolic acid and a mixture of glucosides of sitosterol and stigmasterol[6] from *Mollugo hirta* was reported from this laboratory earlier. The present communication reports the isolation from the leaves of the same plant of a new triterpene glycoside, called mollugocin A, whose structure has been established as mollugogenol *A*-3-[α-L-arabinofuranosyl-(1→5)-α-L-arabinofuranosyl-(1→4)-β-D-glucopyranoside (**1**).

The ethanolic extract of the defatted plant material (*M. hirta*) on concentration and keeping overnight at room temperature yielded a colourless crystalline material. This on repeated crystallization from EtOH (95%) gave a saponin, $C_{46}H_{78}O_{17}$, mp 276–80° (dec), $[\alpha]_D^{27}$ −12·2° (Py) which was homogeneous by TLC, mollugocin A (**1**).

Acid hydrolysis of (**1**) with ethanolic HCl yielded mainly mollugogenol A [1,2] and traces of 22-dehydro-



(**1**)

mollugogenol A [1,2] and mollugogenol B [3] which were artefacts formed during the acid hydrolysis. Enzymatic hydrolysis of mollugocin A with β-glucosidase gave only mollugogenol A. Controlled acid hydrolysis with ethanolic sulphuric acid gave L-arabinose and D-glucose, in the ratio of 1:2 as shown by GLC.

The methylated aglycone $C_{32}H_{56}O_4$, mp 201–3°, obtained after hydrolysis of the permethylated product [7] with methanolic HCl did not show the molecular ion peak in the MS, but showed peaks at *m/e* 486 $(M\text{-}H_2O)^+$ and *m/e* 446 $(M\text{-}58)^+$ and an intense peak