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COMPOSITAE

STEROLS OF *LACTUCA SATIVA* SEED

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Plant. Lactuca sativa (lettuce, cv. Grand Rapids). *Previous work.* GLC separation of derived acetates of sterols from seed.[1]

Present work. The following sterols from seed (Page Seed Co., New York) have been characterized by GLC (OV-17) and GC–MS[2,3] as their derived TMS ethers: campesterol (14% of sterol fraction), stigmasterol (12%), sitosterol (52%), Δ^5-avenasterol (4%), stigmast-7-en-3β-ol (12%), and Δ^7-avenasterol (6%).

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[1] B. A. KNIGHTS, *J. Gas Chromatog.* **2**, 339 (1964).
[2] B. A. KNIGHTS, *J. Gas Chromatog.* **5**, 273 (1967).
[3] B. A. KNIGHTS and C. J. W. BROOKS, *Phytochem.* **8**, 463 (1969).

Key Word Index—Lactuca sativa; Compositae; sterols; sitosterol; campesterol; stigmasterol; stigmast-7-en-3β-ol.

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α-CYCLOCOSTUNOLIDE AND DIHYDRO-β-CYCLOCOSTUNOLIDE FROM *MOQUINEA VELUTINA*

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THE SEARCH for sesquiterpene lactones with schistosomicidal activity[1] led us to investigate a number of species of Brazilian Compositae,[2] among them the common arboreal species *Moquinea velutina* Bong. Silica gel chromatography of the oil obtained by extraction of the trunk wood of *Moquinea velutina* afforded two crystalline compounds.

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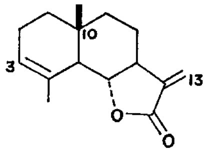
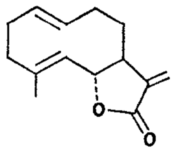
[1] B. GILBERT, J. P. DE SOUZA, C. C. FORTES, F. D. DOS SANTOS, A. DO PRADO SEABRA, M. KITAGAWA and J. PELLEGRINO, *J. Parasitol.* **56**, 397 (1970).
[2] W. HERZ in *Recent Advances in Phytochemistry*, Vol. I (edited by T. J. MABRY, R. E. ALSON and V. C. RUNECKLES), p. 229, Appleton–Century–Crofts, New York (1968).

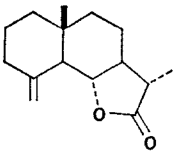
One of these, α-cyclocostunolide (I) m.p. 80–82°, $[\alpha]_D^{24}$ + 116·5° ($CHCl_3$), the principa lactone present was isolated in about 0·05% yield. The α,β-unsaturated γ-lactone group was identified by IR and UV spectrometry, and a pair of doublets at 5·37 and 6·04 δ ($J = 3$ Hz) in the NMR spectrum ($CDCl_3$) suggested the presence of an exocyclic methylene group. A further vinylic proton absorption at 5·35 δ in $CDCl_3$ solution could be shifted clear of the terminal methylene doublet in deuterobenzene. It was associated with an allylic methyl group signal at 1·84 δ ($CDCl_3$), while an angular methyl group also present absorbed at 0·90 δ. A triplet at 3·87 δ ($J = 11$ Hz) due to an axial C-6 proton with two axial proton neighbours, was consistent with *trans* attachment of the five membered lactone ring at C-6, C-7 to a decalin ring system. These data taken in conjunction with the mass spectrally determined molecular formula $C_{15}H_{20}O_2$, were suggestive of a sesquiterpene lactone and in fact further NMR data could be interpreted in terms of structure (I), α-cyclocostunolide, a product previously known as a cyclisation product of the naturally occurring germacrane type lactone costunolide (II).[3,4] Direct comparison with an authentic sample confirmed identity.[5]



α - Cyclocostunolide (I)



Costunolide (II)



Dihydro - β - cyclocostunolide (III)

The second lactone, dihydro-β-cyclocostunolide (III), m.p. 135–137°, $[\alpha]_D^{25}$ + 165° transparent in the UV above 204 nm, exhibited an IR band at 1770 cm^{-1} suggestive of the presence of a five-membered ring lactone. The mass spectrally determined molecular weight corresponded to $C_{15}H_{22}O_2$, corresponding to a structure with one less double bond than was present in (I). In the NMR spectrum a singlet at 0·89 δ and a 3 proton doublet at 1·25 δ due to angular and secondary methyl groups and absorptions due to the non-conjugated terminal methylene group at 4·80 and 4·95 δ were consistent with structure (III), a product previously obtained by cyclization and hydrogenation of costunolide (II).[4] Direct spectral, chromatographic and mixture m.p. comparison with an authentic sample showed complete identity.[5]

EXPERIMENTAL

Collection, extraction and chromatography. The trunk of *Moquinea velutina* Bong. was collected in Espírito Santo and Minas Gerais states, Brazil. Powdered wood and bark (4 kg) was percolated with hexane at room temp. and the percolate evaporated under reduced pressure to give an oil (1·5 kg). Chromatography of this oil (70 g) on silica gel (700 g) gave fractions eluted with hexane–benzene (1 : 1) which partly crystallized.

α-Cyclocostunolide. The crystalline portion of the above fraction was separated and recrystallized from methanol–ether to give α-cyclocostunolide as pale cream-colored needles (420 mg) m.p. 80–82°, $[\alpha]_D^{24}$ + 116·5 (c, 1·02 in $CHCl_3$). IR spectrum ν_{max}^{KBr} 1760, 1650 cm^{-1}, UV, λ_{max}^{EtOH} 208 nm (ε, 11,500), NMR (100 MHz in $CDCl_3$), 0·90 δ (3H singlet, C-10C$\underline{H}_3$) 1·84 δ (3H, singlet with fine structure C-4C$\underline{H}_3$), 3·87 δ (1H, triplet, $J = 11$ Hz, C-6$\underline{H}$), 5·37 δ (1H, doublet, $J = 3$ Hz, C-13$\underline{H}$ superimposed on 1H, broad C-3$\underline{H}$), 6·04 δ (1H, doublet, $J = 3$ Hz, C-13$\underline{H}$). Addition of C_6D_6 shifted the latter absorptions to 5·13 δ (C-13$\underline{H}$), 5·29 δ (C-3$\underline{H}$) and 5·94 δ (C-13$\underline{H}$). The mass spectrum exhibited principal peaks at *m/e*: 232·151382 (41%, $C_{15}H_{20}O_2$), 217 (100%, $C_{14}H_{17}O_2$, M–CH_3), 163 (18%, $C_{10}H_{11}O_2$), 145 (11%, $C_{11}H_{13}$), 121 (11%, C_9H_{13}), 119 (17%, C_9H_{11}), 109 (16%, C_8H_{13}), 107 (31%, C_8H_{11}), 105 (29%, C_8H_9).

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[3] G. H. Kulkarni, G. R. Kelkar and S. C. Bhattacharyya, *Tetrahedron* **20**, 2639 (1964).

[4] T. C. Jain and J. E. McCloskey, *Tetrahedron Letters* 2917 (1969).

[5] Kindly provided by Drs. T. C. Jain and J. E. McCloskey (University of Victoria, Canada) and by Dr. S. C. Bhattacharyya (Nat. Chem. Lab., Poona, India).

Dihydro-β-cyclocostunolide (III) although also present in the above mentioned fraction was obtained more conveniently from a crystalline deposit (1·0 g) in the original crude hexane extract (200 g). Recrystallization from hexane–benzene (4:1) and then from methanol gave dihydro-β-cyclocostunolide (600 mg), m.p. 135–137°; $[\alpha]^{25}_{D}$ + 165° (c, 0·98 in $CHCl_3$). IR spectrum ν^{KBr}_{Max} 1773, 1625 cm^{-1}, UV transparent above 204 nm, NMR (60 MHz in $CDCl_3$) absorptions at 0·89 δ (3H, singlet C-10C$\underline{H}_3$), 1·25 δ (3H, doublet, J = 7 Hz, C-11C$\underline{H}_3$), 4·00 δ (1H, triplet with fine structure, J = 10 Hz, C-6$\underline{H}$), 4·80 and 4·95 δ (two 1H singlets, C-4C$\underline{H}_2$). The mass spectrum showed principal peaks at m/e 234 (100%, M$^+$), 219 (76%), 207 (10%), 192 (29%), 176 (43%), 166 (92%), 138 (48%), 122 (46%), 110 (40%), 108 (40%), 106 (29%).

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Key Word Index—Moquinea velutina; Compositae; sesquiterpenoid lactones; α-cyclocostunolide; dihydro-β-cyclocostunolide.

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β-AMYRIN ACETATE AND CAMPESTEROL FROM *PLUCHEA ODORATA*

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Plant. Pluchea odorata, Hiebp de Santa María. *Source.* La Leona, Nuevo León. *Uses.* Medicinal.[1] *Previous work.* None.[2]

Present work. Aerial part. The plant material coarsely powdered was extracted with light petroleum. A portion was extracted with $CHCl_3$, the solvent was evaporated, the residue was taken into EtOH, and the solution treated with 5% lead acetate. After filtration the EtOH was evaporated and the residue dissolved in $CHCl_3$. The solution was chromatographed on silica gel. *β-Amyrin acetate* $C_{32}H_{52}O_2$; (M$^+$ 468) m.p. 225°, TNM positive, $[\alpha]_{589}$ 69·90°, $[\alpha]_{578}$ 73·70°, $[\alpha]_{546}$ 82·50° ($CHCl_3$) IR, NMR, co-TLC and m.m.p. with an authentic specimen. *Campesterol,* $C_{28}H_{48}O$, m.p. 151°, TNM positive $[\alpha]_{589}$ − 33·3° ($CHCl_3$), IR, UV, NMR, co-TLC and m.m.p. with authentic material. *Acetate,* $C_{30}H_{50}O_2$ m.p. 128–130°; $[\alpha]_{589}$ − 35·2° ($CHCl_3$), IR 1720 (CO) and 1250 cm^{-1} (C–O).

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[2] R. HEGNAUER, *Chemotaxonomie der Pflanzen*, Vol. 3, p. 447, Birkhause, Basilea (1964).

Key Word Index—Pluchea odorata; Compositae; β-amyrin acetate; campesterol.