H, 3·94%; M, 204. All these characteristics agree very well with those of a sample of methylnaphthazarin previously isolated by us from *Euclea lanceolata*[3] and they prove that both substances are the same compound.

The plants of *D. lycioides* were collected near Sá da Bandeira, Angola and herbarium specimens are in the Institute for Scientific Research, Luanda: *D. heterotricha* was collected in Salazar, Angola and specimens are in the University of Coimbra.

Acknowledgements—We are indebted to Dr. R. W. A. Oliver, University of Salford, for the MS and to Dr. V. Santos Gil, Chemical Department, University of Coimbra, for the MNR spectrum.

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Phytochemistry, 1972, Vol. 11, pp. 2353 to 2354. Pergamon Press. Printed in England.

GERANIACEAE

STEROLS AND TRITERPENES OF *PELARGONIUM HORTORUM*

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Key Word Index—*Pelargonium hortorum*; Geraniaceae; sterols; triterpenes; sitosterol; β-amyrin.

Plant. Pelargonium hortorum. Previous work. An unidentified sterol, m.p. 136–137°[1] and monoterpene biosynthesis.[2]

Present work. In conjunction with investigations on the translocation of sterols and triterpenes in plants it was necessary to identify the principal nonsaponifiable constituents of the geranium. This plant is particularly adaptable for laboratory experiments throughout the year, being readily accessible in greenhouse culture. The completely dried flowering plants (385 g) were extracted exhaustively with hot EtOH. The extract was distilled to dryness. A neutral fraction (5 g) was obtained by mild treatment with KOH followed by extraction with Et_2O. The neutral fraction was chromatographed on alumina and separated into hydrocarbons, steryl and triterpene esters, free triterpenes and free sterols. Of the material eluted the esterified sterols (80 mg) accounted for 9% while the free sterols (785 mg) accounted for 91%. The ester fraction was saponified in 15% KOH (benzene–H_2O–EtOH

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[1] F. ESTERNER and K. H. LISHEN, *Arch. Pharm.* **295**, 823 (1962).
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1:1:8) followed by extraction with Et_2O. Both the free and esterified sterols (4-desmethyl) and triterpenes were further purified by preparative TLC on silica gel H (TMP–EtOAc–HOAc; 60:40:0·4 and EtOAc–hexane (1:3) Et_2O–benzene (12:88) 1:4).

Free compounds. Sterols (*4-desmethyl*). GLC (1 % SE-30 and 3 % XE-60) and GLC–MS (3 % OV-17) indicated the presence of, cholesterol (4 %), campesterol (12 %), stigmasterol (6 %), and sitosterol (79 %). The MS of the compound having the same retention time as cholesterol yielded the following fragments: 386 (M^+), 371 (M^+-CH_3), 368 (M^+-HOH), 353 (M^+-CH_3 + HOH), 301 (M^+-HOH + C_5H_7), 275 (M^+-HOH + C_7H_9), 273 (M^+-side chain), 255 (M^+-side chain + HOH), 247, 231 (M^+-side chain + 42), 213. *Triterpenes.* Cycloeucalenol, in trace amounts, was the only 4α-methyl sterol detected by GLC (1 % SE-30 and 3 % OV-17). GLC (1 % SE-30 and 3 % XE-60) and GLC–MS (3 % OV-17) of the 4,4-dimethyl sterol region indicated the presence of β-amyrin (42 %), α-amyrin (28 %), and a compound tentatively identified as isomultifluorenol (30 %). MS of the latter gave the following major fragments, with the relative intensities indicated in parentheses: 426 (M^+), (29 %); 411 (M^+-CH_3), (30 %); 259 (59 %); 247 (47 %); 241 (58 %); 229 (68 %); 218 (45 %); 205 (71 %); 203 (58 %); 137 (88 %); and 109 (100 %). The fragments at *m/e* 218 and 203 may be due in part to contamination by β-amyrin.

Djerassi has conducted extensive mass spectral studies on pentacyclic triterpenes.[3] His spectrum for isomultiflororenone is analogous to our unidentified compound. The fragmentation pattern suggests a baurene type pentacyclic triterpene with a double bond at C-8 and a hydroxyl group at C-3. The relative intensities between fragments *m/e* 205, 247 and 259 is indicative of a double bond at C-8.[3] In our spectrum, however, we also have major peaks at *m/e* 229 and 241. These we attributed to the fragments *m/e* 247 and 259 minus water. In subsequent work we will elucidate the structure of this compound in greater detail. Following acetylation, the triterpene region (4,4-dimethyl sterols) was subjected to preparative TLC on silica gel G impregnated with 12 % $AgNO_3$. GLC analyses indicated the presence of, in trace amounts, cycloartenol acetate and 24-methylene cycloartanol acetate, and confirmed the presence of α-amyrin and β-amyrin as their acetates.

Esterified. Sterols (*4-desmethyl*). GLC (3 % OV-17 and 1 % SE-30) and GLC–MS (3 % OV-17) confirmed the presence of cholesterol (1 %), campesterol (6 %), and sitosterol (93 %). *Triterpenes.* GLC (3 % OV-17 and 1 % SE-30) and GLC-MS (3 % OV-17) indicated the presence of β-amyrin (35 %), α-amyrin (33 %), and the unknown triterpene (32 %) also isolated in the free form. Acetylation of a portion of this fraction followed by preparative TLC on silica gel G impregnated with 12 % $AgNO_3$ and analysis by GLC (1 % SE-30) indicated the presence of trace amounts of obtusifoliol acetate, cycloeucalenol acetate, cycloartenol acetate, and 24-methylene cycloartanol acetate. All spectra and their interpretations were compared with spectra obtained from authentic samples and previous investigations.[3–5]

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