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24-DIHYDRO OBTUSIFOLIOL FROM *SORGHUM VULGARE* CARYOPSES

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Key Word Index—*Sorghum vulgare*; Graminae; phytosterols; 24-dihydro obtusifoliol; seeds.

Plant. Sorghum vulgare Pers. DC 36 or Kaffir Corn. *Source.* Messrs. Gunsons Seeds Pty. Johannesburg, S. Africa. *Uses.* Widely grown as a tropical and sub-tropical cereal crop. *Previous work.* None. *Plant part examined.* The caryopsis or "seed grain".

The caryopses were homogenized and refluxed first in Me_2CO then in a $CHCl_3$–MeOH mixture [1]. This total lipid extract was purified on a silicic acid column, saponified and the triterpenes and sterols isolated from the unsaponifiable lipid by alumina column chromatography. The sterols were then precipitated with digitonin, regenerated with DMSO [2] and purified by further alumina column chromatography [3]. Silica gel TLC, developed with $CHCl_3$, was used to isolate the 4-monomethyl sterols. These were acetylated and further separated by argentation TLC [4] into three bands. Band 1 (R_f 0·38) containing the 4-monomethyl sterols with saturated side chains was eluted and separated by GLC on OV-17,QF-1 and SE-33 columns.

Three compounds were distinguished which were further examined by GLC–MS. This showed two of them to be the acetates of 24-methyl and 24-ethyl lophenol which have been previously reported from larch leaves [5] and grapefruit peel [6]. The GLC and MS data for the third compound shows it to be the acetate of 24-dihydro obtusifoliol. This compound has not previously been reported from a vascular plant although trace quantities have been found to occur naturally in *Chlorella emersonii* [7]. The MS of this third compound shows a typical sterol fragmentation pattern with a molecular ion at *m/e* 470 and the base peak at *m/e* 395 (M^+–Me + Ac). Other important ions at *m/e* 343 (M^+–SC) and *m/e* 283 (M^+–SC + Ac) indicate a sterol with a C_9H_{19} side chain and

Table 1. GLC and MS data on the monomethyl sterol acetates from *Sorghum vulgare*

Sterol acetate	GLC Data RR_t (cholesterol acetate = 1·00)			MS data, *m/e* and relative intensities (%)					
	OV17*	QF1†	SE33‡	Molecular ion	Other major ions				
24-Dihydro obtusifoliol	1·38	1·45	1·38	470 (18)	395 (100)	343 (6)	283 (18)	287 (10)	227 (25)
24-Methyl lophenol	1·66	1·45	1·54	456 (100)	381 (25)	329 (7)	269 (90)	287 (9)	227 (45)
24-Ethyl lophenol	2·10	1·77	1·93	470 (90)	395 (25)	329 (8)	269 (100)	287 (10)	227 (35)

* 3% OV-17; 225°; N_2 flow rate 40 ml/min; RR_t 5a cholestane to cholesterol and cholesteryl acetate 0·37 and 0·26 respectively. † 2·5% QF-1; 205°; N_2 flow rate 25 ml/min; RR_t 5a cholestane to cholesteryl acetate 0·21. ‡ 1% SE-33; 225°; N_2 flow rate 25 ml/min RR_t 5a cholestane to cholesteryl acetate 0·34. All stationary phases used 80–100 mesh gas chrom Q as support.

an additional nuclear methyl group. Ions at *m/e* 287 and 227 show that this methyl group is situated on C-14. The longer RR_t of this compound on QF-1 than on the two less polar phases is additional evidence for the placing of this methyl group [8].

This sterol must possess either a double bond in the nucleus or a 9B-19 cyclopropane ring as it has an M^+ of 470 and a saturated side chain. The absence of an *m/e* 302 fragment indicates a double bond. The RR_t of this third compound is much lower than that of 24-ethyl lophenol which has the same molecular weight and a Δ^7 double bond (Table 1). Conversely, obtusifoliol, which has a Δ^8 double bond has a very similar RR_t to the third compound. This GLC data is taken as positive evidence for the presence of a Δ^8 bond. The MS was also characteristic of a Δ^8 sterol in having few intense peaks.

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