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TRITERPENE METHYL ETHERS FROM PALMAE EPICUTICULAR WAXES

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Key Word Index—*Arecastrum romanzoffianum*; *Butia capitata*; *Orbignya cohune*; *O. phalerata*; *O. speciosa*; Palmae; chemotaxonomy; triterpene methyl ethers; 3-β-methoxy lupane.

Abstract—Cylindrin and lupeol methyl ether were isolated for the first time from Palmae leaf epicuticular waxes. *Butia capitata* and *Orbignya* spp. contain large amounts of ethers, but these are absent in *Arecastrum romanzoffianum*. A new triterpene methyl ether was isolated from *O. phalerata* wax. The new compound was characterized as 3-β-methoxy lupane.

INTRODUCTION

Triterpene methyl ethers have been isolated from a number of plants, in particular Graminae [1, 2], and have been used as taxonomic markers [3]. In Palmae, triterpene methyl ethers have been isolated from fruits [4]. The present paper describes the isolation of triterpene methyl ethers from epicuticular waxes of *Orbignya* spp. and *Butia capitata*, and includes the structural elucidation of a new compound. These results are viewed in terms of the chemotaxonomy of the Cocoid family (Palmae) and the genera *Orbiginia*, which presents some difficulty when attempting to distinguish between early growing species [5].

RESULTS AND DISCUSSION

The leaf epicuticular waxes of *Orbignya phalerata*, *O. speciosa*, *O. cohune*, *Butia capitata* and *Arecastrum romanzoffianum* were analysed by TLC-densitometry [6] and GC. The results shown (Table 1) are the average of four determinations with a standard deviation of less than 5%.

All palm waxes, except that of *A. romanzoffianum*, when developed with toluene on TLC, presented a main fraction (A) at R_f 0.85. These fractions were purified by column chromatography and separated into compounds with ^{1}H NMR peaks at δ3.35 and IR signals at 2820 and 1080 cm^{-1}. These signals can be assigned to a methoxy group. The main fraction of *A. romanzoffianum* epicuticular wax was made up of alkanols (78%).

GC of fraction A from *O. cohune* presented one main peak (> 99.5%, R_t 28 min) with the same mass spectrum as cylindrin [7].

In the case of *O. speciosa* and *B. capitata* the main peak (> 99.5% R_t 27.5 min) was characterized by MS as lupeol methyl ether [2].

Fraction A from *O. phalerata* gave rise to two GC peaks. The first (R_t 27.5 min), had a mass spectrum identical to that reported for lupeol methyl ether [2] and accounted for 97% of the fraction. The second peak (R_t 29.5 min) showed a $[M]^+$ at *m/z* 442 and the typical breakdown pattern of a lupane triterpene with an isopropyl group in ring E (*m/z* 191) [8]. The other peaks were identical to the corresponding lupanes with a shift of 14 of the ions containing the A-ring (methyl ether group). Based on the above evidence the compound was characterized as 3-β-methoxy lupane. It constituted 2% of the fraction.

The fact that triterpene methyl ethers are absent from *A. romanzoffianum* wax is interesting from a chemotaxonomic point of view, as all the palms studied belong to the Cocoid family, indicating a different enzyme specificity between *A. rommanzoffianum* and *Butia–Orbignya* spp. In *Butia* species the alkanol plus triterpene methyl ether fractions represent 60–80%. Alkanols account for 78% of the *A. rommanzoffianum* epicuticular wax.

EXPERIMENTAL

^{1}H NMR: 100 MHz, $CDCl_3$, TMS as int. standard; GC-MS: Hewlet Packard system; GC: HP5890 with HP-1 capillary column (60°, 1 min, 10° min^{-1} to 290°) and a Quadrupolar HP5989A: scan mode between *m/z* 40 and 650 in EI (70 eV, 2000 V detector, source temp. 170°). IR: KBr; TLC: pre-coated (Merck 5554). All solvents were redistilled from glass prior to use. TLC plates were read at 450 nm using a Shimadzu CS-9000 TLC densitometer.

The Palmae voucher codes and origins of the origins needs are as follows: *Orbignya cohune*, FTG 74-124C,

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Table 1. Composition of waxes (% by TLC-densitometry)

	O. phalerata	*O. cohune*	*O. speciosa*	*B. capitata*	*A. romazoffianum*
Hydrocarbons (%)	12	8	10	5	10
Esters (%)	4	6	0	3	5
Fraction A (%)	34	56	85	67	0
Alcohols (%)	26	14	0	8	78
Polar compounds (%)	24	16	5	17	7
Grams of wax per 100 g of leaf	0.27	0.15	0.45	0.44	0.58

Belize; *O. phalerata*, FTG 58-831B, Bolivia; *O. speciosa*, FTG 60-721, Brazil; *Butia capitata*, MVFQ 3504, Uruguay; *Arecastrum romanzoffianum*, MVFQ 3505, Uruguay.

Extraction and fractionation of the wax. Leaves (100 g) were washed with 500 ml *n*-hexane for 30 sec. The solvent was evapd under red. pres. at room temp. and 0.5 g of the residual wax applied to a 100 g silica gel 40 (Merck) column which was then eluted with 500 ml of hexane–benzene (4:1).

Orbignya phalerata, O. speciosa *and* B. capitata. *Fraction A, lupeol methyl ether.* GC: R_t 27.5 min; MS *m/z*: 440, 393, 222, 189; NMR: δ4.68 (*d*), 3.35 (*s*), 2.63 (*m*), 1.71 (*s*).

Orbignya phalerata. *Fraction A, second component* (3-β-*methoxy-lupane*). GC: R_t 29.5 min; MS *m/z* 442, 395, 222, 191, 189.

Orbignya cohune. *Fraction A,* (*cylindrin*). GC: R_t 28.0 min; MS *m/z*: 440, 425, 393, 287, 273.

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