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SECONDARY ALCOHOLS FROM *FRAGARIA* LEAF WAXES

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Key Word Index—*Fragaria chiloensis*; *F. ovalis*; *F. ananassa*; Rosaceae; strawberry; secondary alcohols.

Abstract—The secondary alcohols isolated from *Fragaria* leaf waxes and characterised by GC–MS have been shown to be a mixture of isomers of hentriacontanol with the hydroxy substituent on carbons 9, 10, 11 and 12, and of tritriacontanol with the OH group in the 10, 11, 12, 13 and 14 positions, respectively.

INTRODUCTION

Although secondary alcohols were at one time considered to be less common components of plant waxes, recent reports have shown that they are widely distributed and can constitute the dominant wax fraction [1–5]. Leaf wax secondary alcohols usually consist of a single major homologue with the -OH group commonly located at carbon 10; for a few plants substitution occurs preferentially in the 14, 15 and 16 positions [3]. In contrast, petal waxes contain a wider range of homologues substituted mainly at the 4, 5 and 6 positions [1, 5]. This paper describes investigations of the secondary alcohols of *Fragaria* species which differ from this pattern and yield several constituents which have not been previously identified.

RESULTS AND DISCUSSION

Secondary alcohols were confined largely to the glaucous abaxial surface of *F. chiloensis* leaves but were present in almost identical amounts on the adaxial and abaxial surfaces of *F. ananassa* and *F. ovalis* leaves. Hentriacontanol and tritriacontanol, present in almost equal proportions, were the sole constituents of the fractions from all waxes (Table 1). The homologue distribution in this class followed closely the hydrocarbon profile and gave clear support to the proposed biosynthetic pathway for the formation of these oxidation products [6]. Both homologues consisted predominantly of the 11- and 12-isomers, whilst of the remaining constituents, hentriacontan-10-ol and tritriacontan-13-ol were the most prominent. Hentriacontan-9-ol, identified as a minor component in these waxes, has been previously reported as a major component of rose flower wax [1] and a minor constituent of *Exochorda racemosa* leaf wax [3]. The 12- isomer of hentriacontanol and the 10-, 11-, 12-, 13- and 14-isomers of tritriacontanol are here reported for the first time as leaf wax components.

EXPERIMENTAL

Wax extraction. Waxes were removed separately from the abaxial and adaxial surfaces of fresh leaves. The adaxial surface wax was isolated by washing this surface with $CHCl_3$ delivered from a burette. These leaves were then immersed briefly in $CHCl_3$–Et_2O (1:1) to recover the abaxial surface wax.

Isolation of secondary alcohols. The secondary alcohols, identified initially by TLC [7] were recovered as a $CHCl_3$ extract from the band isolated by preparative TLC (Si gel–C_6H_6) [8].

Table 1. Composition of the leaf wax secondary alcohols from species of *Fragaria*

Plant species	% Total wax	Homologue and isomer content (%) C_{31}*		C_{33}*	
F. ananassa cv Red Gauntlet	8	9-ol	1	10-ol	1
		10-ol	14	11-ol	14
		11-ol	21	12-ol	18
		12-ol	25	13-ol	5
				14-ol	1
F. chiloensis	6	9-ol	1	10-ol	2
		10-ol	11	11-ol	22
		11-ol	22	12-ol	20
		12-ol	16	13-ol	5
				14-ol	1
F. ovalis	10	9-ol	tr	10-ol	3
		10-ol	5	11-ol	16
		11-ol	15	12-ol	25
		12-ol	30	13-ol	3
				14-ol	2

* Key fragment ions: C_{31} sec. alc. TMSi ether (*m/e*) $M^+ - 15$ (509), 9-ol (215 + 411), 10-ol (229 + 397), 11-ol (243 + 383), 12-ol (257 + 369); C_{33} sec. alc. TMSi ether (*m/e*) $M^+ - 15$ (537), 10-ol (229 + 425), 11-ol (243 + 411), 12-ol (257 + 397), 13-ol (271 + 383), 14-ol (285 + 369); C_{31} ketone (*m/e*) M^+ (450), 9-ol (141 + 337), 10-ol (155 + 323), 11-ol (169 + 309), 12-ol (183 + 295); C_{33} ketone M^+ (478), 10-ol (155 + 351), 11-ol (169 + 337), 12-ol (183 + 323). 13-ol (197 + 309), 14-ol (211 + 295).

Chromatographic analyses. GC analysis of the TMSi ethers prepared using BSA–C_5H_5N [8] were performed with a Dexsil 300 column using an FID instrument. Homologues were identified by comparison with the retention data of authentic reference compounds. The identity of the positional isomers was resolved from the fragmentation patterns obtained by GC–MS of the TMSi ethers [3] and the ketones prepared by CrO_3 oxidation [5].

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NEUE THIOPHENACETYLENVERBINDUNGEN AUS *CULLUMIA SETOSA**

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Aus der südafrikanischen Gattung *Cullumia* haben wir bisher zwei Vertreter auf ihre Inhaltsstoffe untersucht [1]. Die isolierten Thiophenacetylen-Verbindungen entsprechen weitgehend denen aus *Berkheya*-Arten [2]. Auch die Wurzeln von *C. setosa* R.Br. enthalten Thiophen-Derivate. Neben den bekannten Verbindungen **1**–**3**[2] isoliert man vier weitere, die bisher noch nicht beobachtet wurden. Die spektroskopischen Daten führen zu den Strukturen **4**–**7**. Bei **4** und **5** handelt es sich um zwei Methylether, die sich nur durch die Endgruppe unterscheiden. Die Hauptverbindung hat eine Acetylen-H-Gruppe, während die zweite eine Methylacetylen-Gruppe besitzt. Entsprechend läßt sich **4** als Silbersalz von **5** trennen. Die Massenspektren zeigen, daß die Methoxygruppe endständig angeordnet ist, da nur so die Abspaltung von $^{\cdot}CH_2OMe$ zu deuten ist. Die vorhandene OH-Gruppe muß daher am Nachbar-C-Atom stehen, da die UV-Maxima ein durchkonjugiertes System erkennen lassen. Die ^{1}H-NMR-Spektren (s. Tabelle 1) zeigen, daß 2,5-disubstituierte Thiophene vorliegen, während die relative Anordnung der Dreifachbindungen bzw. des Thiophenringes durch Vergleich der chemischen Verschiebungen mit denen zahlreicher analoger Verbindungen folgt.

Tabelle 1. ^{1}H-NMR-Daten von **4**–**7** ($CDCl_3$, 270 MHz, TMS als innerer Standard)

	4	**5**	**6**	**7**
1-H	—	*s* 2.08	—	*s* 2.08
2-H	*s* 3.30	—	*s* 3.34	—
7-H	*d* 7.11		*d* 7.11	
8-H	*d* 7.16		*d* 7.00	
10-H	—	—	*d* 2.79	
11-H	—	—	*m* 3.79	
12-H	*dd* 4.67		*m* 3.86	
13-H	*dd* 3.62		*d* 3.68	
13'-H	*dd* 3.56			
OMe	*s* 3.47		*s* 3.43	

J(Hz): 7,8 = 3.8; 12,13 = 4; 12,13' = 7; 13,13' = 17; bei **6**/**7**: 10,11 = 5; 12,13 = 6.

Auch bei **6** und **7** handelt es sich um ein Paar, daß sich analog nur durch die Endgruppe unterscheidet. Wiederum folgt die Stellung der Methoxygruppen aus den Massenspektren. Nach Abspaltung von Wasser beobachtet man die zum Basis-Peak führende Abspaltung von $^{\cdot}CH_2OMe$. Wie durch Doppelresonanz-Experi-

*251. Mitt. in der Serie "Polyacetylenverbindungen"; 250. Mitt. Bohlmann, F. und Abraham, W. R. (1979) *Phytochemistry* **18**, 839.