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SHORT REPORTS

ISO-HEPTACOSANE IN TULIP POLLEN AND *ISO*-PENTACOSANE IN LILY POLLEN

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Key Word Index—*Tulipa gesneriana*; tulip; *Lilium* species; lily; Liliaceae; pollen; hydrocarbons; *iso*-heptacosane; *iso*-pentacosane.

In the course of our study on the constituents of tulip flower (*Tulipa gesneriana* L.), we have noticed the presence of an interesting hydrocarbon in the pollen. GLC of a *n*-hexane extract of the pollen showed a very prominent peak between *n*-hexacosane and *n*-heptacosane, but its presence was negligible in the stems, leaves, bulbs and other parts of the flower. The same peak was also characteristic of all tulips we have examined to date, but is seldom detected in the pollen of other plants (see below). Isolation of the compound by column chromatography and fractional crystallizations yielded a hydrocarbon, mp 49–50.5°. GC, MS, ^{1}H NMR and IR spectra suggested that it is *iso*-heptacosane (**1a**) containing a small amount of *n*-heptacosane.

For identification, **1a** was synthesized as follows. Docosanoic acid (**2a**) was converted to the 8-quinolyl ester (**3a**) which on Grignard reaction [1] with *iso*-amyl magnesium bromide gave 2-methylhexacosan-5-one (**4a**) accompanied by *iso*-amyl docosanoate (this may be due to an aerial oxidation of the Grignard reagent). The modified Clemmensen reduction [2, 3] of **4a** afforded **1a**, mp 47–48.5°. GC and mass spectra analysis corroborated its identity with the natural product.

The pollen of eight plants of the genus *Lilium* was then investigated (see Table 1). Their *n*-hexane extracts showed, except for *L. speciosum* (subgenus M), a peak of **1a** of only negligible extent. For *L. speciosum*, **1a** was the most prominent hydrocarbon as for *Tulipa gesneriana*. The most intense peak for the plants of subgenus P (4 *forma* of *L. elegans*) was *iso*-pentacosane (**1b**), identical to the synthetic specimen (synthesized from eicosanoic acid (**2b**) as described in **1a**: **2b** → **3b** → **4b** → **1b**) by GC. However, **1b** was not detected in the plants of subgenus L (*L. regale* and *L. makinoi*) where *n*-pentacosane was the most intense peak. *L. auratum* (subgenus A) showed the intense peaks of *n*-pentacosane and *n*-heptacosane, both

Table 1. Composition of the *n*-hexane extract of tulip and lily pollens

	Hydrocarbons					
Taxon	*n*-23	*i*-25	*n*-25	*i*-27	*n*-27	*n*-29
Tulipa gesneriana						
Asilid			(+)	+++	+	
Eisenhower			+	+++	+	(+)
Adolno		+	(+)	+++	(+)	
Prelidium		++	+	+++	(+)	
Sakura		(+)	(+)	+++	+	
Rose beauty				+++	+	
Lilium elegans						
Ubatama	+	+++	++		+	
Tamajishi	(+)	+++	++		+	
Matsuno-hikari		+++	++	+	+	
Koshiji	(+)	+++	++		+	
L. auratum		++	+++	+	++	(+)
L. speciosum				+++	++	(+)
L. regale	+++		+++	(+)	+	+
L. makinoi	++		+++	(+)	+	+

R_t: *n*-25 (*n*-pentacosane), 2.4 min. *i*-27 (*iso*-heptacosane), 3.4 min. *n*-27 (*n*-heptacosane), 3.7 min.

+++, Most intense peak (100%); ++, peaks of >50% intensity; +, peaks of 20–50% inensity; (+), peaks of 10–20% intensity. Others were omitted.

of which were accompanied by the peaks of **1a** and **1b** with appreciable intensities. Table 1 suggests that the subgenus of *Lilium* plants may be characterized by the GC pattern of the hydrocarbon fraction of their pollen, although further examples must be investigated for a definite conclusion.

Iso-heptacosane (**1a**) is a rare hydrocarbon in nature. Its occurrence in *Cannabis sativa* L. var. *indica* (Moraceae), *Myristica fragrans* Houtt (Myristicaceae), *Balanites aegyptiaca* and *B. pedicellaris* (Zygophyllaceae) has been reported [4, 5]. Accordingly, its prominent occurrence in tulip pollen as a characteristic constituent is particularly interesting.

EXPERIMENTAL

Mps were measured on micro hot-stage mp apparatus and are uncorr. IR spectra were taken as KBr discs and MS spectra were measured at 70 eV. GC as carried out with a FID instrument, using a glass column (2 m × 3 mm ID) packed with 1.5% OV-1 on Shimalite W (80–100 mesh), with N_2 (60 ml/min) as carrier gas. Column temp. 270°, injector temp. 290°. Wako-gel C-200 (Si gel) was used for column chromatography.

GC of n-*hexane extracts of pollen.* Pollen (0.01–0.1 g) was extracted ×3 with *n*-hexane with occasional shaking. The combined extracts were passed through a short column of Si gel and the eluate concd to dryness. The residue was dissolved in *n*-hexane to yield an appropriate concn and directly analysed by GC. The following plants were examined. *Tulipa*: *T. gesneriana* L. (Asilid, Eisenhower, Adolno, Prelidium, Sakura and Rose beauty). *Lilium*: subgenus P *L. elegans* (Ubatama, Tamajishi, Matsuno-hikari and Koshiji); subgenus A *L. auratum*; subgenus M *L. speciosum*; subgenus L *L. regale* and *L. makinoi.*

Isolation of iso-*heptacosane* (**1a**) *from tulip pollen.* The *n*-hexane extract (4.71 g) of the pollen (Asilid, 106 g) was chromatographed over Si gel (4 × 20 Cm) and the *n*-hexane eluate subjected to fractional crystallizations from EtOAc. The least soluble fraction gave colourless scales, mp 56.5–58°, which were identical to *n*-heptacosane (lit. [6] mp 59.5°). MS *m/e*: 380 [$M^{+\cdot}$]. The more soluble fraction gave *iso*-heptacosane (**1a**), mp 49–50.5°, scales from EtOAc. MS *m/e* (rel. int.): 380 [$M^{+\cdot}$] (100), 365 [$M^+ - 15$], 337 [$M^+ - 43$] (70). ^{1}H NMR (100 MHz, $CDCl_3$): δ 0.82–0.85 (Me) and 1.28 (CH_2 + CH), with intensity ratio of 8:48 (for **1a** the ratio is 9:47).

Physical data of synthetic compounds (including new compounds). 8-Quinolyl docosanoate (**3a**). Faintly yellow plates from Me_2CO, mp 67–68°. IR: 1760 cm^{-1}. 2-Methylhexacosan-5-one (**4a**). Colourless needles from EtOAc, mp 58–58.5°. IR: 1700 cm^{-1}. MS *m/e*: 394 [$M^{+\cdot}$]. *Iso*-heptacosane (**1a**). Colourless scales from EtOAc, mp 47–48.5°. MS *m/e*: 380 [$M^{+\cdot}$]. 8-Quinolyl eicosanoate (**3b**). Faintly yellow plates from Me_2CO, mp 63–64°. IR: 1760 cm^{-1}. 2-Methyltetracosan-5-one (**4b**). Colourless needles from EtOAc, mp 52–53°. IR: 1700 cm^{-1}. MS *m/e*: 366 [$M^{+\cdot}$]. *Iso*-pentacosane (**1b**). Colourless scales from EtOAc, mp 41–42°. MS *m/e*: 352 [$M^{+\cdot}$].

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