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Long-Chain Hydrocarbons in the Pollen of Rye

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The chemical composition of pollen grain has been subject to extensive investigations. Several amino acids, carbohydrates, lipids, vitamins, enzymes and even hormones and growth substances have been reported (*cf.* Ref. ¹). From the lipid fraction saturated hydrocarbons, higher alcohols, sterols, fatty acids and trace amounts of some ketone-containing components have been isolated ²⁻⁶.

Several hydrocarbons have been reported: a saturated hydrocarbon (probably nonacosane) in the pollen of "white flint corn" ², a high content of heptacosane in the pollen of sugar beet ³, tricosane in the pollen of hazel (*Corylus avellana*) ⁴⁻⁵. More recently Nilsson, Ryhage and von Sydow ⁶ investigated hydrocarbon mixtures from pollen of maize and alder (*Alnus glutinosa*). Their mass spectrometric analysis of the mixtures showed that maize pollen contained only pentacosane and heptacosane while alder contained heptacosane, nonacosane and traces of tricosane and pentacosane. Small peaks, in the C₂₉ and C₃₁ regions of the spectrum of maize pollen, were not believed to originate from saturated hydrocarbons or alcohols but possibly from unsaturated hydrocarbons.

The present study was devoted to hydrocarbons isolated from pollen of rye (*Secale cereale* L.). The chloroform-methanol extractable material amounted to 10.6 %

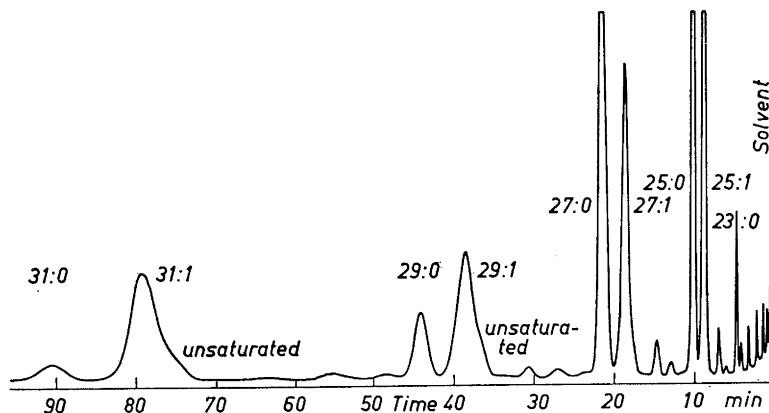


Fig. 1. Gas chromatogram of hydrocarbons in the pollen of *Secale cereale*. Stationary phase: Apiezon L.

and the hydrocarbons to 1.3 % of the weight of the air-dried pollen. The hydrocarbons were separated from other components by chromatography on silicic acid and then submitted to gas-liquid chromatography (GLC). The GLC columns used were of the low-loaded type; the stationary phase amounted to only 1 % of the solid support. Apiezon grease⁷ and methylsilicone elastomer⁸ was used, respectively.

Table 1. The percentage composition (wt) of the hydrocarbons in the pollen of *Secale cereale*.

Number of carbon atoms	Hydrocarbons	
	saturated	unsaturated (mainly monoenic)
18	0.4	
19	0.4	
20	0.5	
21	0.5	
22	0.5	
23	2.0	0.5
24	0.7	0.2
25	12.3	13.7
26	0.9	0.4
27	16.6	13.1
28	0.4	0.5
29	4.2	12.4
30	trace	0.6
31	1.7	16.6
33	—	0.4

The solid support was made inert by means of dimethyldichlorosilane⁹ and any remaining adsorption on active sites in the siliceous material was suppressed by adding a small amount of polyethylene glycol¹⁰. The working temperature of the columns was held at 217–218°. The retention times were much longer on Apiezon than on silicone. A complete separation between saturated and mono-unsaturated hydrocarbons with the same chain-length could be achieved on Apiezon columns of the low-loaded type, see Fig. 1. The unsaturated components emerge from the Apiezon columns before the saturated ones. However, dienes and trienes cannot be separated from monoenes on Apiezon.

Part of the hydrocarbon mixture was completely hydrogenated and the paraffins were identified by semi-log plots using normal paraffins as standards. The main constituents were all odd-numbered with 25, 27, 29 and 31 carbon atoms, see Table 1. The hydrocarbons with 25 and 27 carbon atoms consisted of about equal proportions of saturated and unsaturated components. On the other hand the C₂₉ hydrocarbons contained about three times and the C₃₁ hydrocarbons ten times as much unsaturated as saturated components. Trace amounts of hydrocarbons with retention times different from those of normal hydrocarbons were also found. The more rapid analysis on silicone showed very small amounts of some unsaturated C₃₃ hydrocarbon.

Material. The sample of pollen from rye (*Secale cereale*) was obtained from AB Cernelle, Vegeholm, Sweden.

Air-dried pollen (100 g) was extracted with chloroform-methanol 2:1, in a non-siphoning solid extractor under boiling for several hours. The solvent was then evaporated and the extractable fraction weighed. An amount of 10.6 g (10.6 %) was obtained.

Chromatography on silicic acid. Silicic acid (Baker AR, Lot. No. 23043) with particles passing a 325 mesh sieve was used. The pre-treatment of the silicic acid was the same as earlier described^{11,12}. A 60 g column was packed in light petroleum (b.p. 60–80°) and rinsed with the same solvent. An amount of 1.385 g of lipid material was applied to the column. The hydrocarbon fraction was eluted with light petroleum. The yield was 0.173 g (12.5 %).

Hydrogenation. About half of the hydrocarbon fraction was hydrogenated using Adams' catalyst in an amount of 10 mg in 3 ml of ethyl acetate at 40°. The catalyst was removed by filtration. The completeness of hydrogenation was checked by GLC.

Conditions for gas-liquid chromatography I. **Chromatograph:** Perkin-Elmer, Model 116 equipped with flame ionization detector. **Column dimensions:** 150 × 0.6 cm o.d. aluminium tubing. **Solid support:** Gas Chrom P (100–120 U.S. mesh) Applied Science Laboratories, Inc., Pennsylvania, treated with dimethyldichlorosilane. **Stationary phase:** Silicone elastomer SE-30, General Electric (1 % by weight of the solid support), 0.27 % polyethylene glycol M. 20000 added. **Temperatures:** Injection: 300°. Detector and column: 216°. (All temperatures measured with mercury thermometer.) **Carrier gas:** He at 70 ml/min. Inlet pressure: 1.5 kp/cm². Outlet pressure: atmospheric. **Recorder:** 2 mV; 1 sec; 1.3 cm/min. **Detector:** Flame ionization detector, one flame hydrogen detector, model Bodenseewerk. **Sample size:** 0.10 μl of a diluted solution in carbon tetrachloride. **Analysis time:** About 19 minutes to hentriacontane.

Conditions for gas-liquid chromatography II. **Chromatograph:** See I. **Column dimensions:** 180 × 0.6 cm o.d. aluminium tubing. **Solid support:** See I. **Stationary phase:** Apiezon L grease, manufactured by Metropolitan-Vickers Electrical Co., Ltd., England, (1 % by weight of solid support), 0.1 % polyethylene glycol M. 20000 added. **Temperatures:** Injection: 300°. Detector and column: 217°. **Carrier gas:** He at 80 ml/min. Inlet pressure: 1.8 kp/cm². Outlet pressure: atmospheric. **Recorder:** 2.5 mV; 1 sec; 0.52 cm/min. **Detector:** See I. **Sample size:** 0.15 μl of a diluted solution in

hexane. **Analysis time:** About 90 min to hentriacontane.

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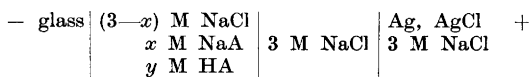
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The Hydrolysis of Sodium Acetate

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Danielsson and Suominen¹ have recently used the cell with liquid junction



to study the hydrolysis of sodium acetate in a 3 M NaCl medium at 20°C. Average degrees of protonation $0 \geq \bar{n}_H \geq 0.1$ for total acetate concentrations $0.3 \geq A \geq 3.0$ M proved to be a unique function of a quantity considered to be $\log [\text{OH}^-]$, and it was concluded that "The hydrolysis . . . is accurately defined by only one equi-