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THE MAJOR VOLATILE CONSTITUENTS OF THE MARMOSET (SAGUINUS FUSCICOLLIS) SCENT MARK

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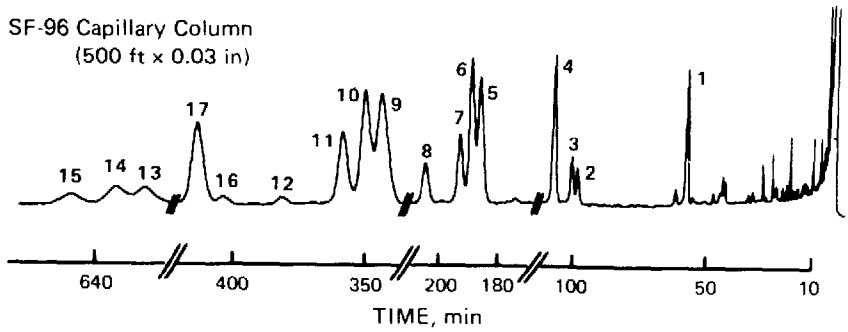
Recently, it has been established that chemical signals play an important role in the social and reproductive behavior of mammals[1] including primates.[2] For example, Epple has demonstrated that the odiferous scent mark[3] deposited by the South American marmoset monkey, Saguinus fuscicollis, communicates to conspecifics a variety of information including the sex, social status, and identity of the donor monkey.[4] As part of our continuing study on the chemical nature and biological function of these scent marks we wish to report here the isolation and identification of the major volatile constituents present in the scent material. Studies concerning the variability of the constituents as it relates specifically to chemical communication will be presented elsewhere.

Initial isolation of the scent material was achieved by allowing preselected animals to deposit their scent onto frosted glass plates. Removal of this material with methylene chloride-methanol (1:1 v/v) and subsequent pooling of individual samples and concentration under nitrogen at 40° resulted in a light yellow oil. Gas chromatographic analysis (SF-96 capillary column: 485" x 0.03")

Identification of the Major Volatile Components in Marmoset Scent Marks



Peak	*Molecular Formula*	*Identification*
		SATURATED
1	$C_{20}H_{40}O_2$	
4	$C_{22}H_{44}O_2$	
8	$C_{24}H_{48}O_2$	
12	$C_{26}H_{52}O_2$	
		MONOENES–TYPE A
2	$C_{22}H_{42}O_2$	
5	$C_{24}H_{46}O_2$	
9	$C_{26}H_{50}O_2$	
13	$C_{28}H_{54}O_2$	
		MONOENES–TYPE B
3	$C_{22}H_{42}O_2$	
6	$C_{24}H_{46}O_2$	
10	$C_{26}H_{50}O_2$	
14	$C_{28}H_{52}O_2$	
		DIENES
7	$C_{24}H_{44}O_2$	
11	$C_{26}H_{48}O_2$	
15	$C_{28}H_{52}O_2$	
		SQUALENE
17	$C_{30}H_{50}$	

of a hexane solution of the oil derived from either male or female donors indicated the common but variable presence of seventeen major components (1-17)[5] representing > 96% (by weight) of the total volatile material.

After purification by micro-preparative gas chromatography[6], tentative structure assignments for the previously unknown components (1-15)[7] were deduced on the basis of their spectral properties, including both low and high resolution mass, infrared and 220 MHz nuclear magnetic resonance spectra. Indicative of the butyrate ester functionality were the mass fragments at M^+, M^+-43, M^+-88 and the base peak at m/e 89[8], while the fact that each ester was a normal butyrate was apparent from its nmr spectrum. To establish the location of the olefinic linkage(s) in the unsaturated butyrates each purified ester was subjected to micro-ozonolysis in carbon disulfide at -65° followed by reductive work-up with triphenyl phosphine[9]. The resultant simple aldehyde fragments were identified by spectral and gas chromatographic comparison with authentic samples, while the aldehyde-ester fragments were assigned on the basis of their mass spectroscopic properties. Assignment of the cis configuration at the olefinic linkage in each case was based on the absence of infrared absorption at 970 cm^{-1}, as well as the inability to observe the trans isomer under chromatographic conditions known to resolve such cis-trans systems.[10] Squalene (17), the only constituent previously known, was readily recognized and identified by comparison with an authentic sample. Finally confirmation of structures (1-15) was obtained by comparison with representative authentic samples prepared by alternative synthesis.

Studies directed at the identification of the more volatile minor components as well as our synthetic work will be communicated in the near future.

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REFERENCES

1. J. Meinwald and E. Muetterties, "Pheromones", in "Methodicum Chimicum", F. Korte, Ed., Vol. XI, George Thieme Verlag, Stuttgart, in press; F. H. Bronson Biol. Reprod. 4, 344 (1971); furthermore several reviews on the behavioral aspects of chemical communication in mammals may be found in "Pheromones", N. C. Birch, Ed., North-Holland Research Monographs Frontiers of Biology, Vol. 32, 1974, North-Holland/American Elsevier.

2. G. Epple in "Pheromones", N. C. Birch, Ed., Vol. 32, North-Holland Research Monographs Frontiers of Biology, North-Holland/American Elsevier, 1974, p. 366.

3. Scent marking is a behavior pattern in which secretions from specialized skin glands in the circumgenital and sternal regions as well as a few drops of urine or vaginal discharge (in the female) are deposited on objects in the environment.

4. G. Epple, Ann. N. Y. Acad. Sci., 237, 261 (1974).

5. All new compounds (1-15) had correct compositional analysis as evidenced either by elemental analysis or high resolution mass spectrometry.

6. Each component was purified by micro-preparative gas chromatography utilizing the Brownlee-Silverstein collection system: R. G. Brownlee and R. M. Silverstein, Anal. Chem., 40, 2077 (1968).

7. Chromatographic fraction (16) appeared to consist of a complex mixture.

8. R. Ryhage and E. Stenhagen, Arkiv för Kemi, 14, 483 (1959).

9. M. Beroza and B. A. Bierl, Anal. Chem., 38, 1976 (1966).

10. Under our infrared and gas chromatographic conditions 5% methyl elaidate was easily detected when added to methyl oleate. Thus the unsaturated esters are > 95% cis.