bottle was then heated to 56° and hydrogen at 50 lb. pressure admitted, whereupon three molecular equivalents of hydrogen were absorbed in 7.6 minutes. The solution, after filtration from the catalyst and decolorization with charcoal, was allowed to crystallize; an additional crop of crystals being obtained after concentration of the mother liquor. The crops were combined and recrystallized from ethanol. The product melted sharply at 129° (cor.) and the yield was 19 g. (90%).

DEPARTMENT OF RESEARCH AND CONTROL
UNITED DRUG COMPANY
BOSTON, MASSACHUSETTS
RECEIVED AUGUST 20, 1943

American Musk. II. A Preliminary Note on the Scent Glands of the Beaver

BY PHILIP G. STEVENS

The recent discovery[1] that cyclopentadecanol and cycloheptadecanol can be obtained in good yields from the scent glands of the common muskrat has prompted an investigation of the scent glands of the beaver. These glands, similar to those of the muskrat in function and shape, but considerably larger in size, have been used for years in the preparation of perfumes. While their odor is not musk-like, the presence of large ring carbinols has not been excluded, and a search for these compounds has now been made.

Walbaum and Rosental[2] studied the steam-distillable fraction of the glandular extract, and obtained therefrom benzyl alcohol, acetophenone, *p*-ethyl and other phenols, benzoic acid and *l*-borneol. St. Pfau[3] confirmed these results in part, but isolated as well an odoriferous lactone of unknown structure, and more recently Yost[4] obtained besides a resin, castorin, cholesterol and an unidentified volatile oil. None of these workers described any large ring compounds, but, since the extracts apparently were not saponified except possibly by Yost, these carbinols may have been overlooked, especially if present, as seems to be the case with 98% of the large ring compounds of the muskrat, as non-volatile esters. The results of saponification experiments described in this note indicate that no large ring carbinols or ketones are present in beaver scent glands. To be sure, the neutral, unsaponifiable fraction yielded a small amount of a viscous yellow oil on distillation with about the correct boiling point of a musk carbinol or ketone, but this oil had the composition $C_{11}H_{18}O_2$ and had a spicy odor, quite unlike musk. On oxidation with chromic acid, the oil gave a product with a cedar-like odor, with, however, no reminiscence of musk.

The acid fraction yielded benzoic acid, various phenolic substances, small amounts of anisic acid,[5] and in addition an amorphous acid, insoluble in benzene and ether, tentatively called castoric acid. Oddly there seemed to be few long chain fatty acids present. This fact coupled with the absence of musk bodies is in sharp contrast to the abundance of fatty acids in the glands of the musk-deer, the civet cat and the muskrat.

Experimental Part

Dried beaver castors (113 g., Fritsche Bros.) were sliced and extracted with ether, and insoluble tarry material was extracted with acetone (1.9 g. of yellow-brown crystalline material which separated from the acetone was not investigated). The solvents were removed from the combined extracts, the dark colored tarry residue (70 g.) was saponified with boiling 10% ethanolic potassium hydroxide, and the neutral products were separated from the acidic. The neutral, red oil (6.3 g.) yielded, after three fractional distillations, 1.5 ml. of a viscous, yellow, unsaturated (rapid bromine absorption from acetic acid) oil, b. p. 147–155° (1 mm.) with a spicy odor. *Anal.* Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 9.9. Found: C, 72.4; H, 9.9. An oil (36.2 g.) similarly prepared from 913 g. of glands (Firmenich & Co.), yielded, after separation of a considerable amount of cholesterol, a distillate, b. p. 86–195° (10–1 mm.), which, combined with similar fractions, was distilled through an efficient column. No pure product was obtained in the range 111–146° (1 mm.) (both boiling point and viscosity increased gradually). The fraction, b. p. 132–141° (1 mm.), had a fine spicy odor, did not react with 2,4-dinitrophenylhydrazine, and on oxidation with chromic acid, gave a product with a strong cedar, but no musk, odor.

The alkaline solution from the saponification was acidified, the precipitated black-red oil extracted with ether, the ether extracted with sodium bicarbonate,[6] the alkaline solution acidified, the liberated acids extracted with ether, and, after removal of the solvent, steam-distilled, yielding 21.5 g. of benzoic acid. The non-volatile residue was dissolved in a large excess of hot sodium carbonate, the cooled solution, after saturation with carbon dioxide, was filtered, and the acidified filtrate deposited a dark-colored precipitate which, centrifuged from benzene twice, yielded 36 g. of air-dried castoric acid as a light chocolate powder, insoluble in ether and benzene, but soluble in methanol.

The aqueous solution separated from the castoric acid was extracted with chloroform, the organic solvent removed, the residue steam-distilled, and the cooled aqueous solution of the non-volatile products deposited crystals which after treatment with norite and crystallization from benzene yielded anisic acid, m. p. 178–180° (a mixture with an authentic sample, m. p. 180–181°, melted at 178–180.5°).

---

[1] Stevens and Erickson, THIS JOURNAL, **64**, 144 (1942).

[2] Walbaum and Rosental, *J. prakt. Chem.*, **117**, 225 (1927).

[3] St. Pfau, *Perfumery and Essent. Oil Record*, **18**, 205 (1927).

[4] Yost, *C. A.*, **26**, 4131 (1932).

[5] I am indebted to Professor Werner Bergmann for help in the identification of the anisic acid.

[6] The separations were made difficult by the deposition of tars. There was however no troublesome frothing of any of the alkaline solutions, indicating the absence of any long chain fatty acids.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.
RECEIVED OCTOBER 15, 1943

Preparation of Malononitrile

BY ALEXANDER R. SURREY

Malononitrile can be prepared by the dehydration of cyanoacetamide with phosphorus pentachloride, by the fusion of the dry materials.[1] This method is not satisfactory for the preparation of large quantities of malononitrile inasmuch as very careful manipulation is needed to prevent the violent decomposition of the product during or before its distillation. The following more convenient method has now been perfected.

---

[1] Corson, Scott and Vose, "Organic Syntheses," **10**, 66 (1930).