150 cc. of water, was added gradually with stirring to a mixture of 153.6 Gm. of sodium nitrite, 30 Gm. of powdered copper and 300 cc. of water. The resulting precipitate was filtered off, washed with a solution of sodium hydroxide and then with water, and dried at 110°. After recrystallization from alcohol, the buff-colored product melted at 76°. Yield very poor. Per cent of nitrogen found, 13.69; calc., 13.21.

4-Acetamino-3-aminophenetole.—A thin paste of 44.8 Gm. (0.2 mol) of 4-acetamino-3-nitrophenetole and 265 cc. of hot water was poured in a thin stream into a boiling solution of 388 Gm. of ferrous sulfate in 750 cc. of water. Stronger ammonia water was then added with vigorous shaking to definite alkalinity. After boiling the mixture for five minutes, it was filtered and the filtrate was cooled in ice-water to produce 16.6 Gm. of product melting at 139–140°. Concentration of the mother liquor gave more to bring the total to 22.1 Gm., a yield of 54.3%. The reduction was also performed with aluminum amalgam, with ammonium sulfide and with sodium hydrosulfite, but the yield in each case was smaller. Per cent of nitrogen found, 13.97; calc., 14.43. Hydrolysis of the compound by usual methods gave 3,4-diaminophenetole melting at 71–72°.

3,4-Diacetaminophenetole.—A small quantity of 4-acetamino-3-aminophenetole was heated with an excess of acetic anhydride for a few minutes, then an equal volume of water was added, and the mixture was boiled to expel excess of acid. Upon cooling, white crystals were deposited that melted at 186°. Hydrolysis of these, as in the previous experiment, gave 3,4-diaminophenetole melting at 71–72°.

2-Amino-4-nitrophenetole (3).—*o*-Phenetidine (30 cc.) was acetylized with acetic anhydride in the usual way. The product was dissolved in 40 cc. of glacial acetic acid, and 87 cc. of sulfuric acid were added gradually with cooling. To the mixture at 0° was added in small portions a solution of 24 cc. of nitric acid in 36 cc. of sulfuric acid. The whole was then poured into 600 cc. of water, and the resulting precipitate of the acetamino compound, after filtering and washing, was hydrolyzed by heating with hydrochloric acid. This brownish yellow hydrochloride was identified by converting to the amine, melting at 97°.

2-Ethoxy-5-nitrophenylhydrazine.—To 35.7 cc. of 2-amino-4-nitrophenetole hydrochloride (0.164 mol), mixed with 30 cc. of hydrochloric acid and 20 Gm. of ice, were added slowly with stirring 11.8 Gm. of sodium nitrite in 24 cc. of water. The diazonium mixture was added to a cold solution of 114 Gm. of sodium sulfite in 246 cc. of water, previously saturated with sulfur dioxide. The mixture was heated at 60–70° and then for an equal period after adding 26 cc. of hydrochloric acid. After standing over night and further heating, the solution was filtered and an excess of sodium hydroxide was added to precipitate the base, yellow crystals melting at 124.5–125.5°. Yield 30.8% of theory. Per cent of nitrogen found, 19.95; calc., 21.32. Benzaldehyde 2-ethoxy-5-nitrophenylhydrazone, glistening orange crystals melting at 169–169.5°. Acetone 2-ethoxy-5-nitrophenylhydrazone, minute orange crystals melting at 123.5–124°.

1-(2-Ethoxy-5-nitrophenyl)-3-methyl-5-pyrazolone.—A mixture of 6.5 Gm. of 2-ethoxy-5-nitrophenylhydrazine and 6 cc. of acetoacetic ester was heated on a water bath for thirty minutes. The dark red solution solidified on standing to a brown mass, from which 8 Gm. of yellowish crystals were separated, melting at 82–83.5°. Yield 89% of theory. The analysis for nitrogen gave very low results and it is probable that the product is contaminated.

SUMMARY

In attempts to make acetaminoethoxyphenyl derivatives of antipyrine, the following new compounds were prepared: 3,4-dinitrophenetole, m. p. 76°; 4-acetamino-3-aminophenetole, m. p. 139–140°; 3,4-diacetaminophenetole, m. p. 186°; 2-ethoxy-5-nitrophenylhydrazine, m. p. 124.5–125.5°; benzaldehyde hydrazone of the latter, m. p. 169–169.5°; acetone hydrazone m. p. 123.5–124°; 1-(2-ethoxy-5-nitrophenyl)-3-methyl-5-pyrazolone, m. p. 82–83.5°.

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Some of the Constituents of the Tuber of Coqui (*Cyperus rotundus* L.). II. The Volatile Oil

*By Conrado F. Asenjo**

The volatile oil present in the tuber of *Cyperus rotundus* L. is the only constituent of this plant to have been studied chemically in the past. Goebel-Kunze (1) in 1830 reported the presence of a volatile oil in the tuber. The distillation of this oil has been carried out in the Sudan, India and Japan. Its use as a fixative in perfumery has been suggested (2).

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Table I.—Constants of the Volatile Oil of *Cyperus rotundus* L.

Item	Oil from Puerto Rico	Maximum and Minimum Values Reported by Other Investigators	
		Maximum	Minimum
Per cent yield (dry tuber basis)	0.40	1.0	0.45
Density 20° C.	0.9428	1.0944	0.9548
Refractive index 20° C.	1.5070	1.5175	1.4988
Optical rotation	−12.9	+35.5	−19.9
Acid value	1.7	11.3	1.0
Saponification value	22.1	31.4	6.6
Saponification value after acetylation	62.9	105.0	63.3

The first scientific article, devoted to the chemistry of this oil, was written by Joseph and Whitfield (3) in 1922. They determined, the principal constants of an oil obtained in the Sudan. In 1925 Rao, Panicker and Sudborough (4) examined several Indian oils, determining their constants and isolating mixtures of dicyclic and tricyclic sesquiterpenes. Hedge and Rao (5) continued this investigation and, in 1935, isolated for the first time the sesquiterpene-ketone α-cyperone. They also demonstrated the presence in this oil of 1-pinene, cineole and of mixtures of secondary and tertiary alcohols. The structure of α-cyperone has been worked out at Simonsen Laboratory (6, 7). They have also synthesized this compound (8). In Japan Kimura and Ohtani (9) have investigated several samples of the oil distilled in that country.

EXPERIMENTAL

Eight thousand seven hundred and fifty grams of air-dried tubers, obtained in Puerto Rico, yielded 200 Gm. of petroleum ether extractive. This extractive was subjected to steam distillation and 32 cc. of volatile oil were obtained. On cohobating the aromatic water, 3 cc. of oil were recovered, making a total yield of 35 cc., that is, 17.5% of the petroleum ether extractive.

This oil has a faintly camphoraceous terebinthinate odor and a yellow color. The principal constants are reported in Table I.

SUMMARY

1. The literature pertaining to the volatile oil of *Cyperus rotundus* L. is reviewed.
2. The yield and constants of the oil, obtained from Puerto Ricon tubers, have been determined.

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The Chemical Nature of Hesperidin and Its Experimental Medical Use as a Source of Vitamin P— A Review

By Ralph H. Higby[*]

The successful clinical treatment of hemorrhagic purpura, and other disorders arising from abnormal capillary fragility, by the administration of hesperidin, has recently been reported by a number of research workers. Present evidence indicates that this glucoside when administered orally fulfils the function of vitamin P, and can probably be regarded as a precursor of this vitamin. Since hesperidin is not generally well known, either to chemists or to the medical profession, it seemed worth while to review the literature dealing with the occurrence, preparation, properties and medicinal uses of this substance.

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