

## PHYTOCHEMICAL NOTES.\*

## NO. 103. A NEW DIHYDROTERPENE.\*\*

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At the time Wehmer compiled his "Pflanzenstoffe" in 1911, only three species of *Pittosporum* had been subjected to partial chemical investigation, viz.,

*Pittosporum undulatum*, Ventenat, of Australia

*Pittosporum resiniferum*, Hemsley, P. I. and

*Pittosporum pentandrum*, (Blanco) Merrill, P. I.

In 1895 R. Threlfall (1) of Sydney observed the "tangerine-like" odor of the Australian fruit. A sample of the steam distilled volatile oil was sent to W. A. Tilden of London, who later turned it over to the Director of the Wellcome Chemical Research Laboratory. At the request of the latter a larger amount of fresh oil was specially distilled in Australia during December 1905 and January 1906. Power and Tutin (2) report about 4 per cent of *d*-limonene, a small amount of esters of valeric, formic and other acids, about 15 per cent of an optically active sesquiterpene (apparently a new one), palmitic acid and an undetermined phenol, in very small amount, and apparently a trace of salicylic acid. In the light of later investigations one would naturally look for *n*-heptane, but the authors do not report this hydrocarbon. Aside from the possibility that this species does not produce *n*-heptane in the fruit, its absence may be accounted for by the observations of Bacon (3).

In 1909, R. F. Bacon reported on three Philippine volatile oils obtained from *P. resiniferum* and one obtained from *P. pentandrum* (4). The first two oils were obtained by expression and subsequent distillation of the volatile constituents. The author states that the fruits are known as petroleum nuts "because of a fancied resemblance in the odor of the oil to that of petroleum" etc. He himself describes the odor of his first oil expressed from the fruit, collected in the autumn of 1907, as "orange-like." Although the lowest fraction (98–103°) "had a pleasant odor recalling oranges," he states that its properties "leave little doubt of the identity of this compound with heptane."

His second oil was prepared by expression and subsequent steam distillation from fruits collected in December 1908. The volatile oil from this "contained no heptane."

However, the oil distilled directly from fruit (not from the expressed materials), collected in December at the same place at which the fruit from which the first oil had been prepared, yielded an appreciable amount of heptane. Treated with concentrated sulphuric acid and redistilled over sodium, the odor of the heptane fraction reminded the author of diphenyl methane. He identified the *n*-heptane in this case by converting it into its primary bromide and this into the corresponding acetate.

Fraction 150–160° constituted the bulk of the oil and is pronounced as consisting of a dihydroterpene, C<sub>10</sub>H<sub>18</sub>. Its hydrochloride was converted into hexa-

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hydrocymene by means of the Grignard reaction. The position of the double bond in the hydrocarbon, however, was not established.

The oil obtained by steam distillation of *P. pentandrum* (5) is supposed to "consist principally of the same dihydroterpene" found in *P. resiniferum*.

*Pittosporum resiniferum* is the third plant on record that produces heptane. This hydrocarbon was first identified in *Pinus Sabiniana* by Thorp (6) in 1879, and Schorlemmer and Thorp (7) in 1883; and in *Pinus Jeffreyi* by Sadtler (8) in 1879, also by Schorger (9) in 1913. The genesis of this unusual hydrocarbon is of special interest. A biogenetic relationship with the so-called terpenes seems out of the question. The production of heptoic aldehyde from one of the fatty acids of castor oil seemed more suggestive. Hence an attempt to study the fatty oil from the seeds of *Pinus Sabiniana* was made in 1917 (10). The amount of fatty oil obtained was insufficient, however, to study the position of the double linkage in the fatty acids. Moreover, whereas the heptane in *Pinus Sabiniana* is obtained from the trunk, the fatty oil studied had been obtained from the seed. In the *Pittosporum* fruit we have an instance where heptane and fatty oil are produced by more closely related parts of the same organ. Hence a study of the fatty acids of the fruit seemed specially desirable. This was made possible through Professor Patrocínio Valenzuela of Manila who persuaded the Bureau of Forestry of the Philippine Islands to collect fruit, pickle it in alcohol and ship the fruit thus preserved in sealed tin cans to Madison. The first lot of fruits was placed at the disposal of A. J. Schwarz, the second at that of the writer. It is, therefore, to Professor Valenzuela and to the Director of the Bureau of Forestry of the Philippine Islands that we are indebted for the opportunity to carry on the investigation here reported.

#### EXPERIMENTAL PART.

The volatile oil was obtained from the concentrated alcoholic extract by steam distillation. Having been shaken with water to remove traces of alcohol, it revealed the following constants:

$d_{20}^{\circ} = 0.7692$ ;  $n_{D26}^{\circ} = 1.435$ ;  $\alpha_{D23}^{\circ} = 20.02^{\circ}$  for 100-mm. tube and  $40.03^{\circ}$  for 200-mm. tube.

The original oil had a saponification value of 0.67, the acetylated oil one of 8.56. Elementary analysis gave the following results:

Computed for $C_{10}H_{16}O$ .	Found:		
	I.	II.	III.
C = 79.6 p. c.	80.6 p. c.	80.5 p. c.	81.3 p. c.
H = 10.5 p. c.	9.4 p. c.	9.4 p. c.	9.9 p. c.
O = 10.5 p. c.			

These figures reveal the presence of an appreciable amount of oxygenated constituents.

In all 1088 cc. of the oil were available. Inasmuch as the weight of the fresh fruit was not known the exact percentage yield could not be computed. Power and Tutin report 0.44 p. c. for *P. undulatum*. Bacon reports 0.5 p. c. for *P. resiniferum* and 0.2 p. c. for *P. pentandrum*.

The oil was fractionated three times, the last time with a 10-inch fractionation column. The results of the last fractionation, also some of the physical constants of the fractions, are herewith recorded:

Fraction amount.	Cc.	t. Deg.	$d_{20}^{\circ}$ .	$n_{D_{20}}^{\circ}$ .	$\alpha_{D_{20}}^{\circ}$ . Deg.
1	40	79-97	0.687	1.391	+3.88
2	145	97-103	0.685	1.393	+2.18
3	150	103-110	0.695	1.395	
4	112	110-120	0.714	1.406	
5	40	120-130	0.739	...	
6	29	130-140	0.883	...	
7	50	140-150	0.927	...	
8	286	150-154	0.947	1.464	+39.34
9	77	154-156	0.952	...	
Residue	20	.....	...	...	

Most of Fraction No. 8 was collected between 152-153°.

*Fraction 8.*—Bacon states that his fraction 158-160° after redistillation over sodium had the composition of a dihydroterpene,  $C_{10}H_{18}$ , from which, however, he did not succeed in preparing a crystalline derivative. An attempt to prepare a nitrosochloride according to Wallach's original method failed so far as any solid products were concerned, though the blue color of the reaction mixture indicated the addition of nitrosyl chloride. In a second attempt glacial acetic acid was avoided and absolute alcohol with gaseous hydrogen chloride used with the ethyl nitrite. Again a blue color was produced, but no solid nitrosochloride separated. In a third attempt heptane was used as solvent and gaseous  $NOCl$  was passed into the cooled solution. A slight amount of white precipitate was formed even before the reaction mixture had become appreciably blue. The precipitate was removed by filtration and more  $NOCl$  passed into the filtrate. In this manner several crops of crystals were obtained without running the risk of passing in too much  $NOCl$ . The nitrosochloride thus obtained was very unstable. While trying to dry it, the crystals liquefied to a brownish mass.

*Nitrolbenzylamide.*—Having learned that the nitrosochloride, even when successfully prepared, is exceedingly unstable, an attempt was made to prepare the benzylamine base from the freshly precipitated nitrosochloride collected in fractions. At first Wallach's original method was tried. When the alcoholic reaction mixture was poured on ice, an oily substance was precipitated. Shaken out with ether, the oily residue, resulting upon evaporation of the solvent, was purified on porous plate. The solid remaining, after crystallization from alcohol, melted at 148-149°.

In subsequent experiments the reaction liquid was allowed to evaporate. Mixed crystals of benzylamine hydrochloride and "dihydroterpene" nitrolbenzylamide resulted. The former were dissolved in water, the latter dried on porous plate. These melted at 146°. Recrystallized from alcohol they melted at 147-148°.

Two nitrogen determinations according to Gunning's method (11) (with salicylic acid and sodium thiosulphate) yielded 10.9 p. c. and 10.7 p. c., respectively, of N. The computed amount for  $C_{10}H_{18}.NO.NH.CH_2C_6H_5$  is 10.2 per cent.

*Nitrolpiperidide.*—Inasmuch as the menthene nitrosochloride cannot be dried, the equivalent amount of base can only be estimated, and that but roughly. The nitrolamine base obtained was very small in amount and that unsatisfactory. The mother liquid was therefore neutralized with sulphuric acid, the solution evaporated, the residue dried on porous plate and what was left shaken with

water to remove piperidine sulphate. The small amount that was left was again drained on porous plate. When dried, it melted at 159°. The amount was too small for even a nitrogen determination.

Attempts to prepare a crystalline nitrosomenthene from the nitrosochloride gave negative results as did also the attempt to convert any non-crystallizable nitroso menthene into menthylamine.

#### REFERENCES.

- (1) F. B. Power and Tutin, "The Constituents of the Essential Oil from the Fruit of *Pittosporum undulatum*," *Trans. Chem. Soc.* (1906), 1083; *Proc. Chem. Soc.* (1906), 170.
- (2) *Trans. Chem. Soc.* (1906), 1092.
- (3) R. F. Bacon, "Philippine Terpenes and Essential Oils, III," *The Philippine Journal of Science* (1909), 4A, 116.
- (4) *Ibid.*, 116.
- (5) *Ibid.*, 118.
- (6) *Jour. Chem. Soc.*, 35 (1879), 269.
- (7) *Annalen*, 217, 149.
- (8) *Am. Jour. Pharm.*, 51 (1879), 176, 293.
- (9) *Ind. Eng. Chem.*, 5 (1913), 971.
- (10) *JOUR. A. PH. A.*, 6 (1917), 242.
- (11) "Off. Tentative Anal. Off. Agr. Chem." (1925), paragraph 29, page 9.

#### THE HANBURY MEDAL.

The proposal that "the memory of the late Daniel Hanbury should be in some way perpetuated is due to Mr. Thomas Greenish; the exact mode in which it seemed desirable that the project should be carried out is due to Professor Dragendorff. The plan is now definitely before the public. A gold medal (two, when the funds allow) is to be granted every two years for high excellence in the prosecution or promotion of original research in the natural history and chemistry of drugs."

The medal itself will be 2¼ in. in diameter, with a likeness of Daniel Hanbury on one side, and the words "Daniel Hanbury, born 1825, died 1875," and on the obverse a space for the name of the recipient within a wreath, with the words "Awarded for Original Research in the Natural History and Chemistry of Drugs."—From *Chemist and Druggist*, March 15, 1879.

A cut of the Hanbury Medal is shown on page 540.

#### DETERMINATION OF ALCOHOLS IN ESSENTIAL OILS.

T. G. Oberhard and N. A. Kubassow. (*Pharm. Ztg.*, 73 (1928), 839). The various mathematical formulas given in textbooks for the correction and determination of alcohols in essential oils by the acetylation and other

methods are discussed and criticised in the light of experiments made with known quantities of alcohols and esters in presence of a terpene or paraffin. Ultimately the formula

$$A = \frac{M}{20} \times \frac{a}{n} \times \frac{n - 0.021 \times b}{s - 0.021 \times a}$$

is adopted as giving results nearest to the actual quantities. In this, "A" = total alcohols; "M" = molecular weight of the alcohols in question; "n" = weight of oil taken; "b" = number of cc. of semi-normal alcoholic solution of potassium hydroxide used in saponifying the esters in "n" Gm. of oil; "s" = weight of acetylyzed oil; "a" = the number of cc. of semi-normal alcoholic solution of potassium hydroxide used for saponifying the esters in "s" Gm. of acetylyzed oil. About 4 Gm. of the original oil should be weighed off for acetylyzing. For menthol-containing oils the acetylyzing process should be continued for at least seventy-five minutes; those containing thymol or borneol must be acetylyzed for at least one and three-quarter hours. The formula, when modified, can also be applied to other methods. Three tables, composed of many figures and calculations, are given, comparing the results worked by the different formulas, obtained from known weights of the various alcohols and non-alcoholic vehicles.—From *Quarterly Journal of Pharmacy*, October to December.