III. 0.5014 Gm. of florets yielded 0.0552 Gm. of insoluble ash, 0.1049 Gm. of total ash, hence 0.0497 Gm. of water-soluble ash by difference.

Comparison with the ash content of the florets of *Monarda fistulosa* L. reveals that whereas the total ash content of the florets of *M. punctata* L. is about two per cent higher, the water-soluble ash content is lower by one per cent and more. Taking into consideration the totally different types of soil on which these two species grow, *M. punctata* L. on sandy soil and *M. fistulosa* L. on clay soil, this difference may not be without significance. It seems all the more desirable, therefore, to make both a qualitative and quantitative examination of the inorganic constituents and to study them with reference to pigmentation, also to the formation of the monatomic phenols.

The Volatile Oil.—Seventy-two Gm. of air-dried florets were distilled with steam. The aqueous distillate was cohobated four times. The total oil, original plus that from the four cohobations, amounted to 2.7 Gm. or 3.45 p. c. The original oil was light reddish brown in color, that from the first cohobation was light yellow, the oils from the second and third cohobations were reddish brown, and that from the fourth was light brown. The amounts, however, were by far too small in each case for separate investigation, hence they were mixed. The mixed oil was light reddish brown in color and by no means as dark as that distilled from the florets of *Monarda fistulosa* L.[1] The density of the oil was 0.9652 at 22°. Comparison with the densities of original and cohobated leaf oils distilled by Sherk[2] reveals that the density of the floret oil is attained only by cohobated leaf oils, whereas in this case the bulk of the floret oil was not obtained by cohobation.

Dilution with heptane did not cause the precipitation of hydrothymoquinone. While this does not show the total absence of this diatomic phenol, it indicates that but little at most can be present. This is significant in connection with the absence of dark color in the oil.

The aqueous distillate from which the cohobated oils had been separated was fractionated. About 25 cc. of this came over between 73° and 99°. Refractionated in 5-cc. fractions these were tested with alkali and iodine. Four of the fractions yielded traces of a yellowish precipitate and the odor of iodoform.

DIMETHYLPHTHALATE AND OTHER ESTERS OF *O*-PHTHALIC ACID.*

BY J. A. HANDY AND L. F. HOYT.[1]

I. Introduction.—The authors' work on phthalates has been continued with special reference to the physical, chemical and pharmacological properties of dimethylphthalate and its comparison with diethylphthalate on whose properties, detection and estimation we have reported in papers Diethylphthalate I–V (1). The properties of some of the other esters of *o*-phthalic acid have also been determined and tabulated.

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[1] *Ph. Rev.*, 21 (1903), 111.

[2] D. C. L. Sherk, Jour. A. Ph. A., 10 (1921), 97.

* Scientific Section, A. Ph. A., St. Louis meeting, 1927.

[1] Larkin Co., Inc., Buffalo, N. Y.

II. Review of Literature.—Since our paper Diethylphthalate V was presented two articles have appeared on the qualitative detection of diethylphthalate. Wales (2) has developed a technique for the reliable detection of diethylphthalate in drugs containing substances which are liable to give a pseudo-positive test in which basic lead acetate is used to remove interfering substances, followed by elimination of the lead and extraction of the ester with petroleum benzine. Scott and Will (3) have greatly improved the Calvert Test by changing the proportions of phenol and sulphuric acid and by controlling the p_H of the final alkaline solution and indicate that their modified test will detect with certainty 0.5 mg. of diethylphthalate in a sample of suitable size of alcoholic beverages and medicinal preparations.

III. Dimethylphthalate.—The dimethyl ester of *o*-phthalic acid is interesting as a possible alternate substitute for the now extensively used diethylphthalate.

The dimethyl ester is now available commercially at a cost of about $.55 per pound. Examination of commercial samples have shown it to be an oily liquid, odorless, practically colorless, having a boiling point nearly the same as that of diethylphthalate, and an intensely bitter taste like that of the diethyl ester.

Solutions were made up, of both the dimethyl and diethyl esters, in Cologne Spirits containing $^1/_{10}$, $^1/_2$, 1 and 2.5 volumes of the respective esters added to 100 volumes of spirits. The taste of the four pairs of solutions was tested. None of the three observers who made the test could consistently differentiate the two esters at any of the four dilutions.

The 2.5% solutions of both esters in Cologne Spirits were tested *versus* iron by immersion for two months of pieces of iron wire (99.7% Fe), ordinary nails, and cast iron having freshly broken surfaces. The effect of the solutions of the two esters was identical, *i. e.*, no action by or on the iron wire or nails, and discoloration of the solution by the exposed cast iron surfaces.

When a solution of 2.5 volumes diethylphthalate in 100 volumes of alcohol (*i. e.*, 39-B specially denatured alcohol) is diluted with distilled water at room temperature a turbid solution results when approximately twice the volume has been added, the amount necessary to produce this effect being a function of the temperature.

When a solution of 2.5 volumes dimethylphthalate is similarly diluted with distilled water at room temperature, no turbidity results at any dilution on account of the distinctly greater solubility of the dimethyl ester in water. Semi-quantitative tests indicated that dimethylphthalate dissolves in distilled water at 25° C. to the extent of approximately 4 Gm. per liter as compared with a solubility of about 1 Gm. per liter for diethylphthalate.

Pharmacological tests of dimethylphthalate on mice, administered *per os* and by intraperitoneal and subcutaneous injection have indicated that dimethylphthalate while somewhat more toxic than methyl salicylate (used in equal volume as a control) is to be rated as a substance of medium toxicity. The dimethyl ester is apparently only moderately toxic and would function the same way as diethylphthalate as regards noxious taste and as a volatile or non-volatile key in alcohol. In addition, the fact that dimethylphthalate yields about 25% of its weight of methanol when saponified might render alcohol denatured with dimethylphthalate less attractive to the illicit denaturing plant than the present 39-B specially denatured alcohol.

Dimethylphthalate like diethylphthalate and for that matter practically all of the other modifying and denaturing agents, used in specially denatured alcohols, with the possible exception of methyl alcohol can be entirely eliminated from Cologne Spirits (pure alcohol) by suitable, physical and chemical manipulations.

Dimethylphthalate does, however, possess one marked advantage over the diethyl ester as an alternative modifying or denaturing agent for specially denatured alcohols, in that the alcoholic solution of dimethylphthalate does not become turbid on dilution with water. This is a distinct advantage in certain toilet and pharmaceutical manufacturing processes, where a specially denatured alcohol of the type of 39-B might be used.

On the other hand diethylphthalate costs less per pound, weighs about one-half pound less per gallon and is more readily available than the dimethyl ester.

It was the aim of the authors to find a denaturant or modifying agent for alcohol which in itself would not have the alleged poisonous effects of methyl alcohol but would still possess the qualities of easy and positive identification and impossibility of removal of methyl alcohol. While dimethylphthalate does not fulfill all these requirements, it is nevertheless worthy of consideration as a modifying or denaturing agent for alcohols for industrial purposes.

TABLE I.—PROPERTIES OF ESTERS OF O-PHTHALIC ACID.

Ester.	Origin.	Odor.	Taste.	Sp. Gr. 15.6/15.6° C.	B. p. ° C.	Refr. index 20° C.	Free acidity as phthalic acid.
Di-Ethyl[1]	8 Com'l. samples	None	Intense bitter	1.1218 to 1.1261	295° C. at 734 mm.	1.5008 to 1.5020	0.017% to 0.105%
Di-Methyl	E. K. Co. No. 318	Pract. odorless	Intense bitter	1.1938	278–280° C. at 744 mm.	1.5158	1.45%
Di-Methyl	Fritzsche Bros. "Avolin"	Odorless	Intense bitter	Not det'd.	Not det'd.	1.5152	0.08%
Di-Iso-propyl	E. K. Co. No. 991	Faint	Intense sharp bitter	1.0625	286–296° C. with decomp. at 744 mm.	1.4900	0.29%
Di-*n*-Butyl	E. K. Co. No. 1403	Faint	Pract. no taste	1.0467	316–326° C. with decomp. at 744 mm.	1.4921	0.08%
Di-*n*-Butyl	Com'l. Solvents Corp.	Pract. odorless	Pract. no taste	1.0490	316–326° C. with decomp. at 744 mm.	1.4920	0.07%
Di-Isoamyl	E. K. Co. No. T2009	Faint, amyl-type odor	Pract. no taste	1.0220	330–338° C. with decomp. at 744 mm.	1.4871	0.08%
Di-Phenyl	E. K. Co. No. 708	Odorless	Tasteless	Not det'd.	M. P. 72.5° C. B. P. Boils above 370° C. with decomp. at 744 mm.	Not det'd.	0.10%

[1] Data from "Diethylphthalate," by J. A. Handy and L. F. Hoyt, JOUR. A. PH. A., 11 (1922), 928.

IV. Other Esters of O-Phthalic Acid.—In addition to the investigation of dimethylphthalate samples of some of the other esters of *o*-phthalic acid were secured and their properties examined in comparison with the dimethyl and diethyl esters. The results of this examination are recorded in Table I. With the exception of diphenylphthalate which is a white crystalline solid all of the esters examined are oily liquids and either colorless or pale amber in color.

Attention is called to the fact that while the dimethyl, diethyl and di-isopropyl esters of *o*-phthalic acid have an intensely bitter taste, the di-*n*-butyl and di-isoamyl esters representing two of the several possible isomeric esters of the C_4 and C_5 groups are practically tasteless. With the two esters tried, *i. e.*, di-*n*-butyl and di-isoamyl, a very faint bitter taste develops as a "delayed reaction" a minute or more after the ester is tasted which was not observed in the case of the diphenyl ester.

The methyl and ethyl esters distil at atmosphere pressure unchanged but the other esters examined undergo some decomposition when similarly distilled.

The results of Table I show that as the molecular weight of the alkyl substituting group increases, some of the physical properties of the esters show a consistent change; thus the specific gravity and the refractive index tend to decrease and the boiling point to increase as the series progresses from methyl to iso-amyl, the only exception noted being the refractive index of the di-isopropyl phthalate.

The study of the esters of *o*-phthalic acid is being continued and elaborated by the authors and other esters will be investigated as they become available.

BIBLIOGRAPHY.

(1) J. A. Handy and L. F. Hoyt, "Diethylphthalate," JOUR. A. PH. A., 11 (1922), 929; II, *Ibid.*, 13 (1924), 600, 702; III, *Ibid.*, 14 (1925), 219; IV, *Ibid.*, 15 (1926), 454; V, *Ibid.*, 16 (1927), 7.

(2) H. Wales, "Note on the Diethylphthalate Test," *J. A. O. A. C.*, 9 (1926), 476; *Am. J. Pharm.*, 99 (1927), 22.

(3) R. D. Scott and E. G. Will, "A Modified Calvert Test for Diethylphthalate," JOUR. A. PH. A., 16 (1927), 417.

BULGARIAN ROSE OIL INDUSTRY.

The Bulgarian Ministry of Agriculture estimates that for the current year 4900 hectares were planted in roses with an expected yield of approximately 53,610 ounces of rose oil. Although the figures given show a decrease from plantings and production of last year, which amounted to 5142 hectares and approximately 88,775 ounces, it is thought that the final result for 1928 may show only a slight falling off.

DERRIS OR TUBA ROOT—SINGAPORE.

There has been considerable interest shown in derris or tuba root recently. While the island of Borneo is probably the largest source of supply, the Malay Archipelago is a considerable factor in the supply of derris. In 1925 there were 500 acres under cultivation in the four Federated Malay States, and 600 acres in the independent State of Johore.

It is reported that estate owners usually demand a price of about 24 cents per pound for the cultivated product, although buyers in Singapore are able to purchase considerable quantities from native collectors and small cultivators at from 10 to 12 cents per pound. It is understood that the present freight rate on tuba root to New York is $17.00 per ton. Considerable quantities are now being shipped to Australia, where a good demand exists for use as sheep dip.

The most common method employed in shipping derris is to press the ground root into bales. Extracting the toxic properties from the root before shipping has not yet been attempted on a commercial scale. (Consul-General A. E. Southard, Singapore.)