

TABLE IV.

Steam distillation fractions.	Average refractive index.	Minimum refractive index.	Maximum refractive index.	Difference between minimum and maximum values.
1	1.4690	1.4654	1.4753	0.0099
2	1.4681	1.4648	1.4740	0.0092
3	1.4684	1.4646	1.4765	0.0119
4	1.4690	1.4665	1.4750	0.0085
5	1.4687	1.4663	1.4725	0.0062
6	1.4684	1.4670	1.4742	0.0072
7	1.4680	1.4659	1.4728	0.0069
8	1.4680	1.4659	1.4721	0.0062
9	1.4684	1.4667	1.4723	0.0056
10	1.4687	1.4671	1.4731	0.0060
11	1.4688	1.4670	1.4737	0.0060
12	1.4684	1.4671	1.4719	0.0048
13	1.4683	1.4671	1.4710	0.0039
14	1.4687	1.4676	1.4710	0.0039
15	1.4692	1.4680	1.4716	0.0036
16	1.4699	1.4688	1.4720	0.0032

TABLE V.

Boiling-point fractions.	-155°.	155 to 156°.	156 to 157°.	157 to 158°.	158 to 160°.	160°+.
Average sp. gr.	0.860	0.861	0.861	0.862	0.864	0.874
Minimum sp. gr.	0.859	0.859	0.860	0.861	0.862	0.871
Maximum sp. gr.	0.861	0.862	0.863	0.863	0.867	0.880
Diff. betw. min. and max. values.	0.002	0.003	0.003	0.002	0.005	0.009
Average refr. index.	1.4662	1.4668	1.4674	1.4680	1.4687	1.4731
Minimum refr. index.	1.4646	1.4659	1.4668	1.4677	1.4682	1.4731
Maximum refr. index.	1.4671	1.4675	1.4688	1.4690	1.4698	1.4765
Diff. betw. min. and max. values.	0.0025	0.0016	0.0020	0.0013	0.0016	0.0055
Sum total of distillates obt. for given temp.	1.93%	8.94%	23.15%	25.99%	25.49%	14.53%

In Table V the sum total of the distillates obtained for the six boiling-point fractions is also given. Less than 10 per cent. of the entire volume of this particular sample of turpentine consisted of pinene, or the fraction boiling at 155 to 156°; three-fourths distilling between 156 and 160°.

In conclusion, the data submitted show the relation between the several fractions, the results being in close agreement with the theoretical valuation. Slight discrepancies are noted but these are of minor consideration.

CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.*

IV. ON CYMENE FROM THE OIL OF *MONARDA PUNCTATA* L.

BY J. M. JOHNSTON, H. MERRITT, AND R. E. KREMERS.¹

Introduction.—Among the plants whose volatile oil contains thymol is *Monarda punctata* L. It grows on poor sandy soil in nearly all states east of the Mississippi River. In the north at least it is often found associated with open stands of oak or jack pine. Hence this species of *Labiatae* deserves careful attention in connection

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with the utilization of non-agricultural lands for forest purposes. The thymol, for which the oil is now valued, is seldom present to an extent of more than 50 per cent. The original investigation of this oil revealed the fact that cymene was the major constituent of the non-phenol portion.¹ It has since been found that other hydrocarbons are present.² With larger quantities of material available, it was thought desirable to attempt the purification of cymene from this source. As is well known the same substance from different sources often requires slightly different methods of isolation and purification. It is hoped that a more complete knowledge of this material may aid in the future production of this oil from forest areas and its subsequent utilization.

Material.—The material used in the following experiments comprised two fractions of non-phenol *Monarda punctata* oil for which we wish to thank the Director of the Wisconsin Pharmaceutical Experiment Station. The two liters of oil represented as many fractions of oil obtained by Mr. Max Phillips by the steam distillation of a large quantity of oil. The following constants were recorded:

Liter no.	d.	n.	α .
11	0.848	1.478	+6.43°
17	0.865	1.481	+6.31°

Fractionation.—Fifty cc of Liter II were submitted to fractional distillation through a short column.

Fraction.	B. p.	Vol. 1st.	Vol. 2nd.
1	160–65°	5 cc	6 cc
2	165–70	10	13
3	170–75	20	26
4	175–80	15	5

The following constants were recorded after each distillation:

Fraction	1	2	3	4	Cymene
d, 1st	0.798	0.846	0.843	...	0.855
n, 1st	1.472	1.477	1.481
n, 2nd	1.469	1.476	1.483	1.485	1.4845
α , 1st	+2.94°	+5.37°	+7.90°
α , 2nd	-2.18°	+4.20°	+8.18°	...	$\pm 0.0^\circ$

It thus became evident that the cymene fraction tended to become more strongly dextro-rotatory by the removal of a lower boiling levo-rotatory substance. This pointed to the presence of a compound of nearly the same boiling point as cymene. Hence it was decided to try chemical purification.

Purification by Permanganate.—A larger portion of Liter II was fractionated as before. Fifty cc of the 170–75° fraction were then oxidized with 1 per cent. permanganate solution by shaking the liquids together at room temperature. Permanganate was added until its color was permanent. The mixture was then steam-distilled until no more oil came over. The latter was separated, dried over sodium, and distilled. The material boiled between 172° and 175° C.

$$d_{23} = 0.8550; n_{23} = 1.4845; \alpha = \pm 0.0^\circ$$

The sulphoneamide prepared from this product according to Schorger's³ method was first thoroughly dried and then melted at 114°.

¹ Schumann and E. Kremers, *Pharm. Rev.*, 14, 223, 1896.

² N. A. Wakeman, *Science*, 51, 397, 1920; *C. A.*, 14, 3643, 1920.

³ A. W. Schorger, *J. Ind. Eng. Chem.*, 10, 258, 1918.

Encouraged by these results, 100 cc of fraction 170–75° were treated as in the preceding case, except that sodium sulphate was used to dry the recovered oil. The latter was resolved into the following fractions:

Fraction.	B. p.	Weight, Gm.	d_{20} .	n_{20} .	α .
1	-173°	5.8	..	1.4838	..
2	173–175	35.1	0.853	1.4852	+6.9°
3	175–177	2.5	..	1.4861	..

Because of its optical activity, Fraction 2 was again subjected to the same treatment, but the resulting 25.5 grams of oil possessed identically the same constants as before the second treatment.

Notwithstanding the discrepancy in rotation, this material was treated with chlorsulphonic acid and converted into cymene-sulphonchloride. From the latter, the following compounds were prepared:

N-phenyl Cymene-sulphone-amide.—This compound was prepared by dissolving one mole of cymene sulphone chloride in *n*-heptane and adding two moles of aniline. The reaction took place instantaneously with the formation of a precipitate. This was filtered by suction, washed with water, and twice recrystallized from 50 per cent. alcohol. The melting point was then sharp and constant at 127–28° C.

N-alpha Naphthyl Cymene-sulphone-amide.—This compound was prepared by mixing one mole of cymene sulphone chloride and two moles of alpha-naphthylamine. Solution first took place, followed by reaction as evidenced by evolution of heat and formation of a precipitate. The solid reaction cake was extracted with ether, which removed the new compound. Alpha-naphthylamine hydrochloride remained as a residue; it was identified by its solubilities, crystal form, and melting point. The impure amide left by the evaporation of the ether was purified by two recrystallizations from 95 per cent. alcohol. M. p., 103–4° C.

N-cymyl-2 Cymene-sulphone-amide.—The amino-2 cymene used in this preparation was obtained by Mr. W. A. DeMonbreun from thujone oxime by Semmler's method. The base and the cymene sulphone chloride were brought into reaction in a manner analogous to the Schotten-Baumann technique. The resultant oil crystallized on standing over night and was purified by recrystallization from alcohol. M. p., 117–18° C.

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VOLUMETRIC DETERMINATION OF SODIUM SALICYLATE.

BY M. W. EVANS.

There has been considerable work done on this subject. Messinger and Vortmann originated the method,¹ and different variations have been used up to that used by J. M. Wilkie, given in *J. Soc. Chem. Ind.*, 1911, page 398. He claims many advantages for this modification. The following results, Table 1, were obtained, carrying out his method with the exception that 50 cc water were used instead of 150 cc. Good results were obtained in several cases, while impossible ones in others, with no apparent reason for the divergence of results, except the uncertainty of the end-point.

TABLE 1.

DETERMINATION OF SODIUM SALICYLATE BY METHOD GIVEN BY WILKIE IN *J. Soc. Chem. Ind.*, 1911, p. 398.

Wt. sample.	No. cc. iodine.	N/10 factor.	Cc sodium thiosulphate.	N/10 factor.	Cc N/10 I ₂ used up.	Factor for sodium salicylate.	Wt. sod. salicylate calculated.	Per cent. sod. salicylate.
0.04004	30	1.0402	14.88	1.0929	14.95	0.0026674	0.039878	99.59
0.04004	30	1.0402	14.77	1.0929	15.07	0.0026674	0.040198	100.39
0.04004	30.17	1.0402	14.80	1.0929	15.21	0.0026674	0.040571	101.33
0.04004	30	1.0385	14.75	1.0929	15.04	0.0026674	0.040118	100.19
0.04008	30	1.0325	14.57	1.0929	15.06	0.0026674	0.040171	100.23
0.04008	30	1.0325	14.43	1.0929	15.21	0.0026674	0.040571	101.23
0.04008	30	0.9567	12.35	1.0929	15.20	0.0026674	0.040544	101.16
0.04008	32	0.9567	14.10	1.0929	15.20	0.0026674	0.040544	101.16

¹ *J. Soc. Chem. Ind.*, 1900, p. 568.