

In all other respects this Toxin-Antitoxin Mixture is the exact counterpart of the usual Diphtheria Toxin-Antitoxin of this strength and it is used in the same dosage, and method of administration for active immunization.

This product offers opportunity for immunization of all subjects hypersensitive to horse serum protein.

PHYTOCHEMICAL NOTES.*†

No. 102. THE NON-HEPTANE CONSTITUENTS OF JEFFREY PINE.

BY P. A. FOOTE.

Early in 1927 an understanding was reached with Dr. Graham Edgar of the Ethyl Gasoline Corporation of Yonkers, N. Y. in accordance with which a large amount of Jeffrey Pine oil was to be sent to the Wisconsin Pharmaceutical Experiment Station for rectification of its principal constituent, the heptane. The non-heptane constituents were to be used for further investigation of these substances whereas the heptane fraction was to be forwarded to Yonkers for the study of the standardization of gasoline as fuel in internal combustion engines. The Jeffrey Pine oil was produced in California during the summer of 1927 as a cooperative enterprise between the Ethyl Gasoline Corporation, the local representative of the Bureau of Forestry and a third party, the California Chemical Company. The material, four drums of about 50-gallon capacity each, was received in the fall of the same year.

Through the kindness of Professor O. Kowalke, the Walter Lummus 20-gallon copper, steam-jacketed alcohol rectifying still of the Chemical Engineering Department was used. It is equipped with a 6-ft. 12-section column and dephlegmator, the latter being unnecessary for this work. The details of this fractionation have been recorded in a report submitted to Dr. Edgar, hence need not be repeated here. The densities of the numerous fractions revealed that great care had been exercised in excluding contamination with Western Yellow Pine. For the purposes of this paper it may suffice to record the summary of materials obtained, *viz.*:

- I. An aqueous cohobate.
- II. Oily fractions distilling below the boiling point of *n*-heptane.
- III. The heptane fractions forwarded to the Ethyl Gasoline Corporation.
- IV. Oily fractions distilling above the boiling point of *n*-heptane after the removal of aldehydes by shaking them with a concentrated solution of sodium acid sulphite.
- V. The oily aldehydes regenerated from the sodium acid sulphite addition products.

Isolation and Identification of the Aldehydes.—From the numerous fractions distilling over above the boiling point of *n*-heptane the aldehydes were removed by shaking them with a concentrated solution of sodium acid sulphite. The solid addition product was separated with the aid of a force filter and the drained solid washed with petroleum ether. The aldehydes were regenerated with sodium car-

* From Scientific Section, A. P. H. A., Portland meeting, 1928.

† From the laboratory of Edward Kremers.

bonate and separated by steam distillation. In this manner 1142 Gm. of material were obtained. The aqueous sulphite mother liquid (not the petroleum ether washings), when made alkaline with sodium carbonate, yielded additional 152 Gm. upon distillation. The two products were kept separate.

The 1142 Gm. of aldehydes were fractionated under a pressure of about 0.1 mm. The melting points of several thiosemicarbazones not being sharp, refractionation under the same pressure was resorted to, this time with a Vigreux column. More than fifty fractions of one degree each were thus obtained. Yield, densities and melting points of thiosemicarbazones are recorded in the following table:

No.	B. p., ° C.	Sp. gr. at 24° C.	Wt. in Gm.	Remarks.
1	to 43	7.6	
2	43-4	0.8193	92.7	Thiosemicarbazone, m. p. 94-95° (softens at 92°)
3	42-3	0.8226	71.2	Slight pressure change
4	43-4	26.3	
5	44-7	13.6	
6	47-8	45.1	
7	48-9	7.3	
8	49-50	5.5	
9	50-51	11.3	
10	51-2	0.8250	77.7	Thiosemicarbazone, m. p. 90-95°
11	52-3	8.6	
12	53-4	14.1	
13	54-5	7.7	
14	55-6	2.0	
15	56-7	0.8324	33.7	
16	57-8	8.0	
17	58-9	4.0	
18	59-60	3.5	
19	60-62	4.0	
20	62-3	0.8267	22.7	Thiosemicarbazone, m. p. 75-77° (softens at 73°)
21	63-4	7.8	
22	64-5	3.4	
23	65-6	13.0	
24	66-7	12.0	
25	67-8	0.8541	39.6	
26	68-9	12.5	
27	69-70	12.4	
28	70-1	0.8595	41.7	Thiosemicarbazone, m. p. 97-98°
29	71-2	20.0	
30	72-3	32.6	
31	73-4	0.8563	108.8	Thiosemicarbazone, m. p. 99-100° (softens at 96°)
32	74-5	22.3	
33	75-6	7.1	
34	76-7	6.8	
35	77-8	0.8558	46.5	
36	78-80	6.5	
37	80-1	35.5	
38	81-2	2.5	
39	82-3	5.8	
40	83-4	1.0	

No.	B. p., ° C.	Sp. gr. at 24° C.	Wt. in Gm.	Remarks.
41	84-97	6.8	
42	97-8	10.7	
43	98-9	8.3	Yellow color of decomposition begins
44	99-100	0.8532	13.5	
45	100-105	6.5	
46	105-110	8.2	
47	110-120	3.4	
48	120-130	2.8	
49	130-135	4.7	
50	135-140	6.1	
51	140-147	21.2	
52	147-157	2.8	
53	157-167	7.0	
54	167-177	2.2	
55	177-185	2.5	
56	Residue	11.9	
Total			1023.0	

In 1913 Schorger¹ working with the oleoresin suspected citronellal. Schimmel & Company² in 1914 found no citronellal but *n*-decylic aldehyde. They also suspected the lower homologues, *n*-octylic and *n*-nonylic aldehydes. The m. p. of the thiosemicarbazones prepared by them are here recorded for comparison.

FRACTION No. 2.

	Found.	Recorded for <i>n</i> -octylic aldehyde.
Boiling point.	43-4° at 0.1 mm. (62-3° at 10 mm. estimated)	60-63° at 10 mm.
Sp. gr.	0.8193 at 24°	0.8211 at 20°
M. p. thiosemicarbazone ³	94-5°	94-5°
n_D	1.4241 at 25°	1.41955 (temp. not given)
α_D	+0.05° at 25°	0°

This fraction corresponds to *n*-octylic aldehyde in the above properties, but is evidently slightly contaminated as is indicated by the slight angle of rotation. Although it absorbs a small amount of bromine, this property may be accounted for by partial enolization.

FRACTION No. 20.

	Found.	Recorded for <i>n</i> -nonylic aldehyde.
Boiling point	62-3° at 0.1 mm. (80-82° at 13 mm. estimated)	80-82° at 13 mm.
Sp. gr.	0.8267 at 24°	0.8277 at 15°
M. p. thiosemicarbazone ⁴	75-77°	77°
n_D	1.4432 at 25°	1.42452 at 16°
α_D	+0.10° at 25° C.	0°

¹ *Ind. Eng. Chem.*, 5, 971.

² *Ber. v. Schimmel & Co.* (Apr. 1915), 48.

³ Using a 25-p. c. excess of reagent on 0.7826 Gm. of the fraction the yield was 74.5 p. c. of the theoretical assuming the aldehyde to be *n*-octylic.

⁴ Using a 25-p. c. excess of reagent on 0.8379 Gm. of the fraction the yield was 61.5 p. c. of the theoretical, assuming the aldehyde to be *n*-nonylic.

This fraction would, therefore, appear to be largely *n*-nonylic aldehyde. Slight traces of impurities are indicated by the angle of rotation.

FRACTION NO. 31.

	Found.	Recorded for	
		<i>n</i> -decylic aldehyde.	citronellal.
Boiling point	73-4° at 0.1 mm. (93-94° at 12 mm. estimated) ¹	93-94° at 12 mm. 80-81° at 6.5 mm.	89-91° at 14 mm.
Sp. gr.	0.8563 at 24°	0.8361 at 15°	0.8554 at 17.5°
M. p. thiosemicarbazone ²	99-100°	99-100°	54-55°
n_D	1.4480 at 25°	1.42977 at 15°	1.4481
α_D	+1.30		+8.18° to 12.30° ³

This fraction likewise absorbs bromine. The b. p. is close to that of both of the suspected compounds. The sp. gr. and index of refraction are close to citronellal but its optical rotation is small for the latter. Since the melting points of the thiosemicarbazones of *n*-decylic aldehyde and citronellal lie so far apart the m. p. found would indicate that only *n*-decylic aldehyde reacted with the reagent.

The data obtained for Fraction No. 31 were at first puzzling for its b. p. and the m. p. of its thiosemicarbazone were those of *n*-decylic aldehyde, yet its sp. gr. and index of refraction were very close to those of citronellal. The problem was solved several weeks later when the sp. gr. of all the fractions was found to have increased as well as their index of refraction. Polymerization had taken place. When purified by NaHSO₃ the regenerated aldehyde had a sp. gr. of 0.8260 at 25° C. and an index of refraction of 1.4278 at 25° C. Its thiosemicarbazone melted at 99° C. It is therefore *n*-decylic aldehyde.

The absorption of bromine may be explained as due to the enol form of aldehyde, a well-known phenomenon.

The 152 Gm. of mixed aldehydes regenerated from the sulphite liquor upon fractionation gave:

No.	B. p., ° C. at 0.1 mm. Hg.	Sp. gr. at 24° C.	Wt. in Gm.
1	45-52	0.7925	44.3
2	52-6	0.8256	50.1
3	56-62	0.8536	12.0
4	62-68	0.8813	9.8
5	68-73	0.9033	14.3
6	73-100	11.3
		Total	141.8

CONCLUSIONS.

n-Octylic, *n*-nonylic and *n*-decylic aldehydes have been identified.

¹ The variation appears to be 2° per mm. whence the estimations are made.

² Using a 25-p. c. excess of reagent on 4.2212 Gm. of the fraction the yield was 58.9 p. c. of theoretical, assuming the aldehyde to be *n*-decylic.

³ Citronellal from Java lemon oil, -3°.