[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY AND OF LENOIR RHYNE COLLEGE]

A Chemical Examination of the Volatile Oil of Sarothra Gentianoides L. and the Detection Therein of Normal Nonane[1]

BY MARSTON TAYLOR BOGERT AND SIMON J. MARION

The solid members of the paraffin series are quite widely distributed in the plant kingdom, where they often appear as waxy coatings or excretions on various parts of the plant. Naturally, because of their relatively high boiling points, they are not so often found in the volatile oils obtained from these plants by distillation, although occasionally they are present in sufficient amount to cause the oil to congeal at temperatures but little below the normal, as is the case with the atar of rose, for example.

Of the liquid paraffins, on the other hand, the only one definitely identified as a plant constituent is the *n*-heptane which has been reported in the *Pinus sabiniana* and *Pinus jeffreyi* of California and in the "petroleum nuts" of the *Pittosporum resiniferum*, from the Philippine Islands. Brooks, in his well-known volume on "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Inc., New York, 1922, remarks (p. 89) that "Normal heptane enjoys the distinction of being the only saturated hydrocarbon, other than the solid paraffins, formed by phytochemical processes."

It has been reported[2] that the crude wood turpentine produced by the destructive distillation of the longleaf pine contains pentane, but this report lacks confirmation.

Some six years ago, the late Dr. Emerson R. Miller[3] described a preliminary investigation of the volatile oil of *Hypericum perforatum*, in the course of which he collected a low-boiling fraction, whose properties were such as to suggest the presence therein of an aliphatic hydrocarbon not hitherto discovered in any essential oil. Based upon our own results, as recorded beyond, with a closely related species, it seems to us quite probable that Dr. Miller was right in believing that this low-boiling fraction from *H. perforatum* consisted largely of a nonane,[4] although of course this still remains to be proved.

The family of the *Hypericaceae*, containing some ten genera and over 300 species, includes the well-known St. John's Wort, or *Hypericum*, genus, of which only *H. perforatum*, as noted above, seems to have been studied to any extent, either pharmacologically[5] or chemically. From the days of Dioscorides, who lived about the first century A. D., the St. John's Worts

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(1) Presented before the Division of Medicinal Chemistry, at the Meeting of the American Chemical Society, Washington, D. C., March 28, 1933.

(2) Parry, "The Chemistry of Essential Oils," Scott, Greenwood & Son, London, 1921, I, p. 17

(3) Miller, *J. Am. Pharm. Assoc.*, **16**, 824 (1927).

(4) Private communication to the junior author.

(5) (a) Lang, *Schweiz. Apoth. Ztg.*, **70**, 521–523 (1932); (b) Alther, *ibid.*, **70**, 615–618 (1932); *Chem. Abstracts*, **27**, 2532 (1933).

have been popular domestic remedies, having been used for a remarkably extensive list of ailments. Concerning the species *Sarothra gentianoides* L. (*H. sarothra* Michx.), one authority[6] records it as "a much used laxative, alterative, and vulnerary, under the names of Pineweed, False St. John's Wort, Orange Grass and Nitweed."

In the summer of 1923, the junior author, working with Dr. E. R. Miller at the Auburn (Ala.) Experiment Station, made a preliminary examination of a volatile oil obtained from *Sarothra gentianoides* L. but, due to the resignation of the junior author from the staff of the Experiment Station and the death of Dr. Miller, this investigation was suspended until a few years ago, when it was resumed as a coöperative undertaking by the chemical laboratories of Lenoir Rhyne College and Columbia University.

Collection and Distillation of the Plant.—The material used was collected in late August and early September, in the years 1925–1929, inclusive, and mostly in the neighborhood of Hickory, Catawba County, North Carolina.

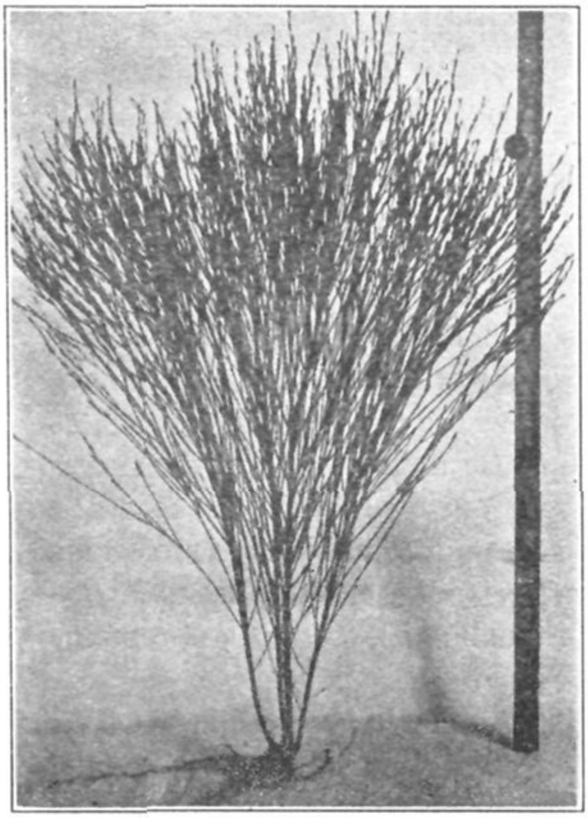

Plate I.—*Sarothra gentianoides* L., in full bloom.

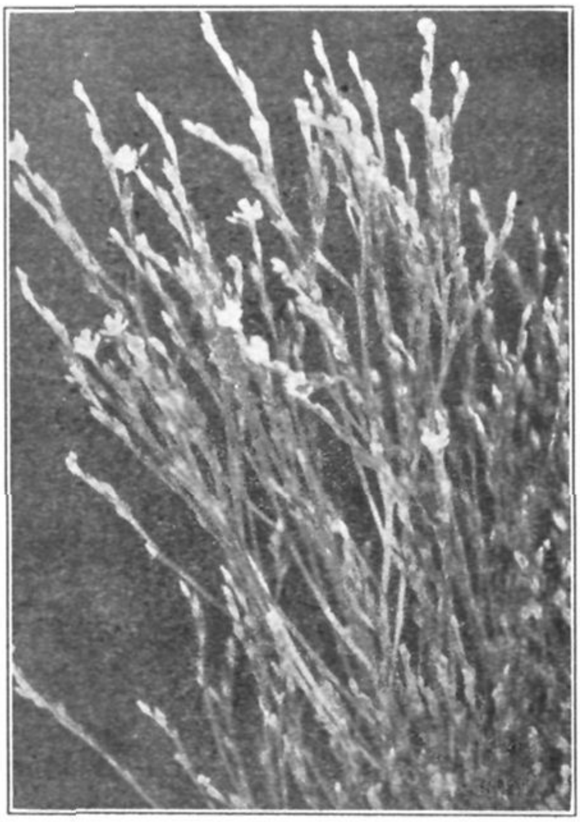

Plate II.—*Sarothra gentianoides* L., enlarged bushy top of plant, showing details of flowers.

The plants were pulled up by the roots, shaken to remove adhering dirt, examined carefully as to species, and all foreign matter removed. The entire fresh green herb, tops, stems and roots, was distilled with steam in

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[6] Millspaugh, *Am. Medicinal Plants*, I, Sec. 30 (1887).

100-lb. lots for periods of about three hours. The yield of volatile oil which separated in the distillate varied from 0.072 to 0.222%, for different years, due probably to different climatic conditions during the growing season. The general average yield of filtered oil, unwashed and undried, was approximately 0.1 to 0.2%, based on the weight of the fresh whole green plant.

The distillations carried out in 1925 are shown in Table I and it will be observed that the yields from the whole green plants, while not uniform, are consistently higher than the 1926 average of 0.098%. It is believed that this is due principally to the plentiful rainfall during the growing period, for we have noted that higher yields of oil are always obtained from the herbs gathered from low moist meadow land. It is possible that the better yield of oil in 1925 (as compared with 1926) may have been influenced somewhat also by the fact that the 1925 distillations were carried out with smaller lots.

During the season of 1925, distillations were also made on different portions of the plants, both fresh and dry. On August 27, 49 lb. of the whole fresh green herbs was collected and the bushy tops cut off, and the two portions, tops and roots, distilled separately. The 49 lb. gave 41 lb., or 83.6% of tops, and 8 lb., or 16.4% of roots and coarse stems. The tops gave a yield of 50.4 g. of oil, and the roots and coarse stems only 1.7 g. Therefore, 96% of the oil is localized in the tops of the plants, representing 83% of the mature herb.

TABLE I

1925 DISTILLATIONS

Date	Material, lb.	Yield, g.	Yield, %
	(1) Whole Green Plants		
Aug. 26	156.0	103.0	0.145
Sept. 17	15.0	15.0	.220
Sept. 19	21.0	21.1	.222
		Av. % yield...	.196
	(2) Green Tops Alone		
Aug. 27	41.0	50.4	0.217
Sept. 2	67.0	103.2	.339
Sept. 18	15.0	21.7	.318
		Av. % yield...	.291
	(3) Dry Tops Alone		
Sept. 17	11.0	13.2	0.264
Sept. 17	10.0	8.3	.183
Oct. 8	9.0	12.3	.301
		Av. % yield...	.249

As mentioned above, the average yield of oil obtained from the harvest of 1926 was only 0.098%, probably because of the very hot dry summer.

During this same 1926 season, a quantity of material was allowed to dry from ten days to four weeks in a cool, dry shed, spread out in a thin layer so as not to heat. In this drying, the herbs lost about 70% in weight, as well as some of the volatile oil, so that when distilled the yield of oil averaged only 0.095%, calculated to the dry basis. The only marked difference between this oil and that distilled from the green plants was that it was darker and had a more pronounced pinene odor.

An acre of plants was raised from seed sown in the spring of 1926 and harvested in August, 1927, but the yield of oil was no better than from the wild herb growing under similar climatic conditions.

The largest amount of material collected in any one season was in 1929, when nearly two tons were distilled and approximately two liters of filtered oil obtained.

Examination of the Oil.—The oil used for the following examination was distilled from the entire green plants—tops, stems and roots. It was filtered, washed thoroughly with water and then dried over anhydrous sodium sulfate.

Its color lay in the Green-Yellow zone, between Normal Tones and Tint 1, of the Bradley Color Standard. Its odor was agreeable, recalling that of oranges, with a slightly balsamic suggestion. It was soluble in chloroform, carbon tetrachloride, ether or absolute alcohol. Cold concentrated sulfuric acid changed its color first to a yellow, then to a purple and finally to a dark red. Cold concentrated nitric acid changed it first to a yellow, then to a dark red, with dark particles floating at the junction of the two liquid layers. It was unaffected by concentrated hydrochloric acid either hot or cold. The only effect produced by glacial acetic acid was to dissolve the oil. Neither cold nor hot 3 N sodium hydroxide caused any change in the color of the oil. Neutral potassium permanganate solution, or an equal volume of a 5% solution of bromine in carbon tetrachloride, was instantly decolorized by the oil. At $-17°$ the oil did not congeal, but assumed a slight milkiness which cleared up at $+5°$.

The following constants were determined: d^{20}_{20} 0.7665, n^{20}_{D} 1.4262, $[\alpha]_D$ +6.39, A. V. 0.58, S. V. 4.43, Ester No. 3.85, S. V. after acetylation 17.35.

Fuchsine and phenylhydrazine tests showed the presence of only traces of aldehydes or ketones. Further, the tests for phenols indicated that they also were present only in minute amount, if at all.

Following a qualitative examination for various elements, a combustion was run on the oil with this result: C, 84.03; H, 14.75; O, 1.22.

It was obvious from these results that the oil must consist mainly of hydrocarbons.

Fractionation of the Oil.—After removal of phenols, aldehydes, ketones, acids and esters, by the usual methods, from 360 cc. of the original whole green oil, the residual oil was washed, dried over anhydrous sodium sulfate and distilled four times with a 4-bulb Young fractionating column. Table II records the results obtained, compared with the constants of the original oil itself.

An examination of this table will disclose several unusual features. In the first place, 70% of this hydrocarbon oil distilled below 150°, and over 60% between 145 and 150°. This fact, taken in conjunction with the exceptionally low density of the oil and the other constants already recorded for the whole green oil, made it seem most likely that Fractions 1, 2 and 3, consisted mainly of acyclic hydrocarbons. Further, it was very significant that the only common volatile oils, of known composition, whose sp. gr. are lower than that of the *Sarothra* oil, are those from *Pinus sabiniana* (d_{15}, 0.6962–0.6971) and *Pinus jeffreyi* (d_{15}, 0.695–0.711), both of which consist principally of n-heptane. The density of the *Hypericum perforatum* oil, mentioned at the beginning of this paper, was reported by Miller[3] as 0.8065 to 0.8180 at 15°.

TABLE II

	B. p., °C.	d^{20}_{20}	n^{20}_{D}	$[\alpha]_D$	No. cc.
Whole green oil		0.7665	1.4262	+6.39	360
Fraction 1	140–145° at 758 mm.	0.7265	1.4071	+ 4.05	25
Fraction 2	145–150° at 758 mm.	.7366	1.4129	+ 7.52	210
Fraction 3	40–60° at 8–10 mm.	.7687	1.4278	+18.96	33
Fraction 4	60–110° at 8–10 mm.	.8014	1.4453	+ 7.46	13
Fraction 5	110–125° at 8–10 mm.	.8927	1.4892	− 9.77	30
Fraction 6	125–140° at 8–10 mm.	.9073	1.4844	− 4.75	8
Residue	Above 125–140° at 8–10 mm.				15
				Total	334
				Loss in handling, etc.	26
					360

Inasmuch as Fraction 2 of the above table represented over 60% of the distillate, had the characteristic odor of the plant and obviously contained the major portion of the low-boiling constituent, preliminary qualitative experiments were conducted with it, as well as some elementary analyses. The results of these experiments and analyses, taken in conjunction with the physical constants noted in the table, indicated that the major constituent of this fraction was a paraffin, probably a nonane, mixed with some olefin, perhaps a nonene or decene.

Isolation and Identification of *n*-Nonane.—As our interest lay primarily in the isolation and identification of this paraffin, a larger quantity of the oil, freed as far as possible from oxygenated compounds by suitable treatment, was repeatedly distilled and a fraction b. p. 146–152° at 735 mm. was collected. This was washed with concentrated sulfuric acid as long as it colored the acid, then with concentrated nitric acid, followed by water, dilute sodium carbonate solution, and water again. After being dried over anhydrous sodium sulfate, it was refluxed for two hours over metallic sodium and then repeatedly fractionated over the same material, finally taking the cut which boiled at 148.5–149.5° (corr.) at 735 mm. A calculation based on Craft's formula, $dt = KT_{BO}\ (760 - P)$, and assuming that the liquid is non-associated, gives a boiling range of 149.5–150.5° at 760 mm.

A number of fractionations, therefore, were carried out with the oil distilled in different seasons from the whole green plant, and yields of 14–20% were obtained of a fraction of this b. p. (149.5–150.5°).

TABLE III

	Sarothra nonane	*n*-Nonane
B. p. at 760 mm., °C.	149.5–150.5	149–151
F. p.,[7] °C.	−60	−51 to −53.68
Sp. gr.	0.7177 at 20/20	0.717–0.738
n^{25}_{D}	1.4025	1.4025–1.4165
$[\alpha]_D$	Inactive	Inactive
Heat of combustion[8]	1.488 Cal.	1.462 Cal.
Mol. wt.	129.9	128.2
C%	84.20	84.27
H%	15.74	15.73

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(7) This was carried out in the laboratory of Dr. H. D. Crockford, Department of Physical Chemistry, University of North Carolina, Chapel Hill, N. C., to whom we are most grateful.

(8) We owe this determination to the courtesy of Professor E. E. Randolph, Department of Chemical Engineering, North Carolina State College, Raleigh, N. C.

Bearing in mind the fact that nearly 60% of the whole green oil distilled at temperatures not exceeding 150°, and that the narrow *n*-nonane cut (b. p. 149.5–150.5°) amounted to 14–20%, a conservative estimate would be that the original oil from the whole green plants contains at least 20% of *n*-nonane.

The carefully purified fraction referred to above, b. p. 148.5–149.5° at 735 mm., or 149.5–150.5° at 760 mm., was optically inactive, and in all its chemical reactions (potassium permanganate, bromine solutions, etc.) behaved like a paraffin hydrocarbon. The product was analyzed and various constants determined.

Table III gives the results side by side with those which appear in the literature (or are calculated).

Synthesis of *n*-Nonane.—As a further check upon the identity of the paraffin hydrocarbon isolated from the *Sarothra* oil, *n*-nonane was synthesized for purposes of comparison, by the method of Clarke and Adams,[9] condensing *n*-heptaldehyde first with ethylmagnesium bromide, hydrolyzing the product to the nonanol, converting this into the corresponding iodide, removing hydriodic acid from the latter by the action of strong alcoholic potassium hydroxide and catalytically reducing the nonene to nonane.

The synthetic *n*-nonane so obtained possessed the following constants: b. p. 149.5–150.5° at 760 mm., d_{20}^{20} 0.712, f. p. −51°, n_D^{25} 1.4055. In other respects it likewise appeared to be identical with the nonane isolated from the *Sarothra* oil. No change in boiling point could be detected when the two were mixed.

Other Hydrocarbons Present in the Oil.—Having isolated and identified the *n*-nonane in Fraction 2 of Table II, this same fraction was examined for olefins, inasmuch as its behavior with potassium permanganate and with bromine indicated clearly the presence of unsaturated hydrocarbons.

A portion of the oil was oxidized by potassium permanganate, the alkaline solution, filtered from precipitate and separated from unoxidized oil, acidified with dilute sulfuric acid and the acid solution distilled with steam. The silver salt prepared from the distillate contained 41.65% silver (average of four determinations), as compared with 41.67% silver in silver caprylate.

From the same distillate the sodium salt of the acid was prepared, and its aqueous solution exhibited a levo rotation of $[\alpha]_D$ −15.8°.

From another portion of Fraction 2, oxidized by chromic acid, an acid was obtained whose silver salt contained 52.19% silver. Silver valerate contains 51.64% silver.

The two acids isolated as oxidation products of Fraction 2, hence, seem to be valeric and active caprylic. These acids could have been formed either from a single tridecene, carrying its olefin bond between carbons 5 and 6, or from 2 different olefins, one a pentene and the other an octene. The latter is the more likely, in view of the physical properties of Fraction 2, the identification of caprylic acid in the whole green oil, and the fact that octene, C_8H_{16} (b. p. 123–124°; *d* 0.7275; n_D 1.4066), is the only olefin which has been detected in essential oils.

Preliminary tests indicate that the higher-boiling fractions shown in Table II are probably made up mainly of terpenes and sesquiterpenes, but this part of the investigation is still unfinished.

Oxygenated Constituents of the Oil.—Preliminary experiments were carried out also on the oxygenated constituents of the oil. Although the amount of material available was in most cases insufficient for conclusive results, these experiments are recorded for the benefit of other workers and because it is uncertain when this investigation can be resumed.

Reference to Table II showed that these constituents could not total more than 16.5% and, as noted above, the elementary analysis of the original oil disclosed only 1.22% (by difference) of total oxygen.

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(9) Clarke and Adams, THIS JOURNAL, **37**, 2536 (1915).

Free Acids.—After shaking 750 cc. of the whole green oil with excess of a 3% sodium bicarbonate solution, the aqueous solution was separated, concentrated, acidified with dilute sulfuric acid, extracted with ether and the ether extract evaporated. The residual dark brown oil, of hircin odor, was dissolved in dilute sodium hydroxide and the silver salt prepared therefrom. This salt darkened and apparently suffered some decomposition on drying, which would make the analytical figures for silver too high. Ignition of the dry salt showed the presence of 49.63% of silver. The silver content of silver valerate is 51.64%, and of silver caproate 48.39%. The presence of caproic acid, therefore, is indicated.

Esters.—The saponification value (4.43) determined on the original oil showed the presence of a small percentage of ester. Some of the oil, therefore, after removal of phenols, aldehydes, ketones and free acids, was saponified with $N/2$ alcoholic potassium hydroxide. The alkaline solution was separated, concentrated, acidified with dilute sulfuric acid, and the acid solution distilled with steam. The distillate had an acid reaction and yielded a silver salt containing 41.69% of silver. The silver salt of caprylic acid contains 41.67% of silver.

Alcohols.—From Fraction No. 5, Table II, there was prepared, by the method of Wallach,[10] a nitroso chloride, which melted at 106.5°. The melting point recorded in the literature for the nitroso chloride of *l*-α-terpineol is 107–108°, and the odor and other properties of this fraction resembled those of liquid α-terpineol.

The constants noted in Table II for Fraction No. 6 corresponded fairly well with those of geraniol. Some of this fraction, hence, was oxidized by a chromic acid mixture, as recommended by Beckmann,[11] and the odor of citral was immediately evident, and the oily product behaved toward the Schiff reagent like citral itself.

Phenols.—Free acids were removed from the oil by agitation with dilute aqueous sodium bicarbonate. The undissolved oil was separated, extracted with a 3% potassium hydroxide solution, the alkaline extract acidified with dilute sulfuric acid and shaken with ether. Evaporation of the ether extract left a small quantity of a brownish residue, of vaseline-like consistency, from which a 3,5-dinitrobenzoate, m. p. 207° (uncorr.), was prepared by the method of Phillips and Keenan.[12]

Aldehydes.—After removal of acids and phenols, the oil was shaken with a 40% sodium bisulfite solution, the bisulfite extract separated and hydrolyzed by boiling with sodium carbonate, and the liberated aldehyde collected with ether. Removal of ether left a very small quantity of an oil, which gave a deep red with the Schiff reagent, and yielded a crystalline semicarbazone, m. p. 105–106° (uncorr.), when dissolved in 30 parts of glacial acetic acid and treated with a solution of 4 parts of semicarbazide hydrochloride in a little water, a P_H at which ketones do not form semicarbazones so readily.

It is worthy of note that the melting point of *n*-caproic aldehyde (*n*-hexanal) semicarbazone has been reported as either 106°,[13] or 114.5–115°.[14]

Ketones.—A qualitative test on the original oil indicated the presence of a trace of ketone. A small sample of the oil, from which acids, phenols, aldehydes, etc., had been removed, as described above, was treated with a solution prepared from 50 g. of semicarbazide hydrochloride, 50 g. of sodium acetate, a small amount of water and sufficient ethyl alcohol to make a homogeneous mixture. After standing for three days, some crystals separated which, after recrystallization from alcohol, melted at 231–232° (uncorr.). Camphor semicarbazone melts at 236–238°. The amount of material we had available was not enough for its positive identification.

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(10) Wallach, (a) *Ann.*, **277**, 120 (1893); (b) **360**, 90 (1908).

(11) Beckmann, *ibid.*, **250**, 325 (1889).

(12) Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

(13) (a) Bagard, *Bull. soc. chim.*, [4] **1**, 319 (1907). (b) McRae and Manske, *J. Chem. Soc.*, 488 (1928).

(14) *Schimmel's Ber.*, Apr., 79 (1913).

Summary

1. The volatile oil of *Sarothra gentianoides* L. consists largely of liquid acyclic hydrocarbons, of which at least 20% is *n*-nonane, a compound which has not hitherto been found in nature.

2. In addition to *n*-nonane, there is evidence of the presence of the following: a low-boiling optically active olefin (probably an octene), unidentified terpenes and sesquiterpenes, α-terpineol, geraniol, traces of phenols, aldehydes and ketones, caproic acid and a caprylic ester.

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Preparation and Dehydration of 4,4-Dimethylpentanol-2 (Methylneopentylcarbinol)

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER[1]

The dehydration of dimethylneopentylcarbinol[2] and of methylethylneopentylcarbinol[3] gives olefins without rearrangement and with dehydration chiefly from the smaller groups. The neopentyl group shows little tendency to supply the proton in the dehydrations. The acid splitting of a C–C linkage in certain olefins having a neopentyl group attached to the ethylenic carbon has been observed.[4] Methyl neopentyl ketone reacts with sodium hypobromite as if it enolized exclusively from the methyl group.[5] Moreover, neopentylethylene adds hydrogen bromide entirely contrary to Markownikoff's rule.[6] In a further study of the neopentyl group, methylneopentylcarbinol has been prepared and dehydrated. Contrary to expectation the dehydration took place mainly from the neopentyl rather than the methyl group, the chief product being 4,4-dimethylpentene-2. No product of any rearrangement was detected.

4,4-Dimethylpentene-2 has been reported by Favorsky and Alexeeva[7,8] who gave its boiling point as 84–86°. Edgar, Calingaert and Marker[9] found that dehydration of 4,4-dimethylpentanol-3 gave a mixture of 4,4-dimethylpentene-2 and rearranged olefins. Boord and Schurman[10] pre-

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[1] Mallinckrodt Research Fellow.
[2] Unpublished results, Whitmore and Wrenn.
[3] Whitmore and Laughlin, THIS JOURNAL, **55**, 3732 (1933).
[4] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).
[5] Homeyer, Whitmore and Wallingford, *ibid.*, **55**, 4209 (1933).
[6] Unpublished results, Whitmore and Homeyer.
[7] Favorsky and Alexeeva, *J. Russ. Phys.-Chem. Soc.*, **50**, 557–570 (1918).
[8] Favorsky and Alexeeva, *C. A.*, **18**, 1466 (1924); *Chem. Zentr.*, III, 998 (1923).
[9] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1487 (1929).
[10] Boord and Schurman, Paper before the Division of Organic Chemistry, American Chemical Society, Washington, D. C., March 28, 1933.