of 3% amalgam required to complete the reduction was 1200 g. An acid was isolated which was quite stable toward permanganate, as would be expected of a tetrahydro acid. The melting point without special purification was found to be 81°, slightly lower than that of tetrahydro-α-naphthoic acid. Results of the titration for the neutral equivalent were as follows:

0.1390 and 0.0916 g. acid = 9.35 and 6.20 cc. 0.085 N alkali. Neutral equivalent found (1) 175 and (2) 174.

The above neutral equivalents agree with the theoretical value (176) for tetrahydro-α-naphthoic acid, indicating that the ethoxy group had been eliminated in the process of reduction.

URBANA, ILL.

ZINGIBEROL—A NEW SESQUITERPENE ALCOHOL OCCURRING IN THE ESSENTIAL OIL OF GINGER.

BY BENJAMIN T. BROOKS.

Received November 18, 1915.

It is a well-known fact that the distilled oil of ginger, *Zingiber officinal* Roscoe, possesses the characteristic aroma of ginger. The odor is not intense, but is very persistent, recalling sandal wood oil in this respect. Gildemeister and Hoffman[1] state "Only a few of the important constituents of ginger oil are known; of the substances which give it the characteristic odor nothing is known."

In the course of an examination of ginger oil which had been freed of terpenes and sesquiterpenes, the author isolated and identified citral, methyl heptenone, nonylaldehyde, linalool, *d*-borneol, acetic and caprylic acids, combined as esters, a trace of a phenol which was probably chavicol though not positively identified, cineol and also a sesquiterpene alcohol, $C_{15}H_{26}O$, which evidently bears the same relation to the sesquiterpene, zingiberene, as santalol does to santalene, and since it imparts to ginger oil the peculiar persistent, though mild, ginger odor, I have called it *zingiberol*. Although all of the constituents of ginger oil contribute something to the composite odor of the fresh root, the alcohol zingiberol is the only one of them possessing the peculiarly characteristic fragrance of ginger.

It should, perhaps, be pointed out that ginger oil does not produce the sharp pepper-like sensation when introduced into the mouth that is produced by the fresh root, and that the so-called "gingerol" claimed by Garnett and Greier[2] to have been isolated by them has no existence in fact. The latter authors did not characterize their gingerol further than that it probably was a phenol and possessed a sharp stinging taste. Fol-

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[1] Gildemeister and Hoffman, "Die Aetherische Oele," Leipsig, **2**, 292 (1913).

[2] *Chem. Zentr.*, **1907**, II, 924; **1909**, II, 1593.

lowing their directions, I isolated from the aqueous alkaline extract, by passing in CO_2, a very small quantity, about 2%, of oil, consisting of a mixture of the sesquiterpene alcohol zingerberol and a trace of a phenolic substance whose taste was phenolic and suggestive of chavicol.

Zingiberol.

From 150 g. of ginger oil, free from terpenes and sesquiterpenes, there were obtained 41.5 g. of oil distilling from 130° to 160° at 14 mm. pressure. By repeated fractionation, this crude fraction yielded 24 g. of oil boiling from 154° to 157° C. at 14.5 mm. Combustion analysis gave:

	Found. Per cent.		Calculated for	
	I.	II.	$C_{15}H_{26}O$.	$C_{15}H_{24}O$.
C..........	80.90	81.54	81.08	81.81
H..........	11.40	11.78	11.71	10.90

The substance is neither a ketone nor aldehyde. Treatment with semicarbazide in the usual manner gave negative results, and an attempt to prepare the oxime resulted in an oil entirely free from nitrogen. Nevertheless, acetylation by heating with acetic anhydride resulted in an oil containing only 17% of ester calculated from the saponification number. Combustion analyses of the acetylated oil also showed that very little dehydration had taken place. Treatment of the substance with phenylisocyanate gave no phenylurethane after standing four days. This fact, together with its behavior to acetic anhydride, indicates that the alcohol is secondary or more probably tertiary. Sodium in dry ether readily forms a sodium compound with the substance, and on gently heating with potassium acid sulfate, water is split off, yielding a hydrocarbon $C_{15}H_{24}$, boiling point 255–257°, and identical with zingiberene or *iso*-zingiberene. Combustion analysis gave:

Calc. for $C_{15}H_{24}$: C, 88.15; H, 11.85. Found: 88.10, 11.41.

Treatment of the hydrocarbon with HCl in glacial acetic acid yielded *iso*-zingiberene dihydrochloride, m. p. 169°.

On treating the alcohol with hydrogen chloride or hydrogen bromide in glacial acetic acid solution and allowing to stand for two days, there are deposited crystals of *iso*-zingiberne dihydrochloride, melting point 169°, or the dihydrobromide, melting point 176°.[1] The dihydrobromide, recrystallized from glacial acetic acid, gave the following analysis:

Calc. for $C_{15}H_{26}Br_2$: Per cent. C, 49.18; H, 7.11; Br, 43.71. Found: 49.11; 7.23; 43.73.

Since zingiberol yields a dihydrochloride and a dihydrobromide identical with the dihydrochloride and dihydrobromide, respectively, of the sesquiterpene zingiberene, it is probable that on treating the alcohol with halogen acids a ring formation occurs, as has been shown by Semmler[2]

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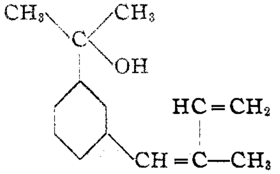
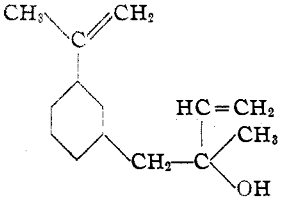
[1] Semmler, *Ber.*, 46, 1822 (1913).

[2] *Loc. cit.*

to be the case with zingiberene. If the constitution advanced by Semmler for zingiberene and *iso*-zingiberene are correct, then the constitution of zingiberol is probably one of the following:



or



In working with ginger oil, the author was much impressed by the rapidity with which resinification occurs. This is particularly true of the pure hydrocarbon zingiberene, which, as Semmler has shown, contains two conjugated double bonds, as in myrcene and isoprene. The author's experience with both the distillation and extraction of fresh vetiver root, the essential oil of which also consists chiefly of sesquiterpenes and their derivatives, proved that better yields of oil were obtained and that the oil was of much superior quality when the roots were distilled or extracted within a few days of their harvest than after storage several months, as must necessarily be the case with roots shipped to Europe for distillation there. It is highly probable, therefore, that distillation or extraction of the freshly harvested ginger rhizomes would give better oil and in relatively larger yields than the dried material usually employed.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

SOME CONSTITUENTS OF SUMBUL ROOT.

BY FREDERICK W. HEYL AND MERRILL C. HART.

Received December 20, 1915.

Since the root of *Ferula Sumbul* is an officially recognized drug of the United States Pharmacopoeia, and has for some years been used as an antispasmodic, it was deemed of interest to subject the root to a more complete chemical investigation. Our present knowledge of its constituents is fairly summarized in the United States Dispensatory[1] where it is stated that the root contains a volatile oil, two balsamic resins, wax, gum, starch, a bitter substance, fat (17%), angelic and valeric acids. Knitl,[2] with Tschirch, isolated umbelliferon. Cushny[3] classifies sumbul with valerian, basing the similarity upon the presence of malodorous volatile oils, which may act psychically and physiologically. Since the oil of sumbul, in consequence of the study of the other constituents re-

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[1] *U. S. Dispensatory*, 19th Ed., 1209.

[2] *Archiv. Pharm.*, **237**, 270 (1899).

[3] "Pharmacology and Therapeutics," 73 (1906).