The benzoyl derivative of the inactive amine was prepared by shaking the amine with benzoyl chloride in a weak potassium hydroxide solution and recrystallizing the precipitate from ethyl alcohol, m. p. benzoyl derivative, 135–136°. *Anal.* Calcd. for $C_{16}H_{16}ONCl$: N, 5.12. Found: N, 5.27, 5.23.

Dextro-α-o-chlorobenzylethylamine.—Twelve grams of *dl-α-o*-chlorobenzylethylamine and 10 g. of *d*-tartaric acid were dissolved in a boiling solution of 100 cc. of water and 100 cc. of ethyl alcohol. The solution was allowed to cool slowly to room temperature and at the end of three days 16 g. of crystals was filtered. This fraction was recrystallized twice from a solution of equal parts ethyl alcohol and water. Seven and one-half grams of the *d*-base-*d*-acid salt was obtained: m. p. 175°; $[\alpha]^{24}_{D}$ (in water *c*, 2.74) +21.1°. *Anal.* Calcd. for $C_{13}H_{18}O_6NCl$: N, 4.38. Found: N, 4.34, 4.48.

The dextro base, regenerated and dried over solid potassium hydroxide gave the following constants: b. p. 75–77° (6 mm.); d^{25}_4 1.0789; α_D +14.9 at 25° in a 1-dm. tube; $[\alpha]^{25}_{D}$ +13.8°; $[\alpha]^{25}_{D}$ (methanol, *c*, 10.3) +11.4°; (hexane, *c*, 13.0) +12.7°.

The hydrochloride of the dextro base gave the following constants: m. p. 175–176°; $[\alpha]^{25}_{D}$ (in water, *c*, 3.78) +9.0°, $[\alpha]^{25}_{D}$ (in methanol, *c*, 8.66) +4.1°.

The benzoyl derivative of the dextro base gave the following constants: m. p. 166°, $[\alpha]^{28}_{D}$ (in ethyl alcohol, *c*, 0.97) 97.6°. *Anal.* Calcd. for $C_{16}H_{16}ONCl$: N, 5.12. Found: N, 5.15.

Catalytic Reduction of Dextro-α-o-chlorobenzylethylamine.—Sixty-three hundredths gram of the pure dextro amine dissolved in 25 cc. of ethyl alcohol and 5 cc. of glacial acetic acid was reduced catalytically using 0.1 g. of palladium oxide catalyst. The catalyst was prepared by the method of Shriner and Adams.[9] The hydrogenation was carried out at room temperature and under six atmospheres of hydrogen for five hours. A test with silver nitrate showed the chloride ion to be present at the end of this time. The solution was filtered and evaporated nearly to dryness on the steam-bath. The amine was liberated with potassium hydroxide and extracted with ether. After the ether was distilled off the benzoyl derivative was prepared by shaking with benzoyl chloride in weak potassium hydroxide solution. The precipitate was recrystallized from alcohol and was shown to be the benzoyl derivative of dextro-α-benzylethylamine by the following constants: m. p. 160°; $[\alpha]^{22}_{D}$ (in ethyl alcohol, *c*, 1.66) +69°; $[\alpha]^{22}_{D}$ (in chloroform, *c*, 3.00) −13.7°. *Anal.* A qualitative test for chlorine was negative. Calcd. for $C_{16}H_{17}ON$: N, 5.85. Found: N, 5.80.

Summary

1. Racemic α-*o*-chlorobenzylethylamine has been synthesized and resolved.
2. Constants of *d*-α-*o*-chlorobenzylethylamine have been reported.
3. *d*-α-*o*-Chlorobenzylethylamine and *d*-α-benzylethylamine have been shown to have the same configuration.

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[9] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

AMES, IOWA RECEIVED FEBRUARY 2, 1938

CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Volatile Oil of Amur Cork Tree Fruit[1]

BY E. K. NELSON

The Amur cork tree (*Phellodendron amurense*), is a native of North China and Manchuria. It was introduced in this country about 1856. The dioecious flowers appear in June and the fruit ripens in September and October.

The fruit, when crushed, has a pronounced aromatic odor, described in some textbooks on botany as "turpentiny."

No record was found in the literature on the constituents of the fruit. Wehmer, "Die Pflanzenstoffe," states that the bark of the tree is used in Japan as a tonic and stomachic, containing about 1.6% berberin besides other constituents.

Fruit for the present investigation of the volatile oil was collected from a heavily bearing tree located in the grounds of the Congressional Library in Washington, D. C. The fruit was collected in October when still green, but on the verge of ripening, and also in November when fully ripe. No difference was found in the composition of the oils from the two lots of fruit, though the ripe fruit gave a somewhat higher yield of oil.

Three kilograms of the green fruit was minced and distilled with steam. Sixty-six cubic centimeters of oil was obtained, a yield of 2.16 cc. per 100 g. of fruit. Eight kilograms of ripe fruit, similarly distilled, afforded 242 cc. of oil, or 3 cc. per 100 g. of fruit. The oil has the following physical characteristics:

Specific gravity 15/15	0.7984
Optical rotation	−.7°
Refractive index at 20°	1.4693

The oil was fractionated at 10 mm. through an efficient column, over 92% boiling at 53–54°, having specific

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[1] Food Research Division Contribution No. 353.

gravity at 15/15, 0.7954, optical rotation, −0.7°, and refractive index at 20°, 1.4705. These figures are close to those recorded for myrcene.

This fraction boils at 164–166° at atmospheric pressure with partial polymerization.

Oxidation with permanganate gave succinic acid, m. p. 186°. Reduction with sodium in alcohol yielded dihydromyrcene (tetrabromide m. p. 89–90°), and hydration with acetic acid and 50% sulfuric acid at low temperature gave myrcenol, having a lavender odor and giving a phenylurethan melting at 71–72°. (Enklaar[2] reported a melting point of 68° for myrcenol phenylurethan.) The phenylurethan from the myrcenol gave sharp depressions in melting point when mixed with both *l*-linalool and *i*-linalool phenylurethans.

The small higher boiling fraction remaining after distillation of the myrcene was redistilled at 10 mm. from a small flask provided with a Vigreux column yielding the following products: (1) a very small fraction, 85–90°; (2) a small fraction, 90–100°; (3) the main fraction, 100–110°; (4) a small fraction, 110–140°; leaving a thick, viscous residue in the flask.

Fraction 1 gave a negative reaction for alcohols on treatment with phenyl isocyanate, but gave a positive reaction for the carbonyl group on treatment with semicarbazide, as did also fractions 2 and 3, which gave copious yields of semicarbazone. On decomposition of the semicarbazones an odor suggesting methyl nonyl ketone was observed.

The semicarbazone from fraction 1 melted at 114.5°. The semicarbazones from fractions 2 and 3 melted at 123–124°, and gave no depression in melting point when mixed with the semicarbazone of methyl *n*-nonyl ketone. While indices of refraction were not measurable in either case, optical crystallographic examination showed identical crystalline form and interference figures.[3]

Fraction 3, boiling at 100–110°, had an odor suggesting geraniol. When a portion of this fraction was oxidized with potassium dichromate, an odor of citral was detected. However, attempts to isolate geraniol as the diphenylurethan, or the semicarbazone of citral, were unsuccessful, due no doubt to the predominance of methyl *n*-nonyl ketone.

From the distillation residue a non-volatile oil was extracted which gives a lasting tingling sensation to the tongue and lips. Alkaloidal material was found only in traces, so this physiological effect is not due to aconitine. This substance is being further investigated.

Summary

The volatile oil of Amur cork tree fruit contains over 92% of the aliphatic terpene, myrcene.

The higher boiling portion of the oil contains methyl *n*-nonyl ketone, with possibly a small amount of a lower homolog such as methyl *n*-heptyl ketone.

Evidence was obtained of the presence of a small amount of geraniol in the fraction boiling at 100–110° at 10 mm.

The slight optical activity of the myrcene fraction is probably due to a small amount of an optically active terpene.

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[2] Enklaar, "Over Ocimeen en Myrceen," Inaugural Dissertation, Utrecht, 1905.

[3] Optical crystallographic examination was made by G. L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

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On the Nature of Pyroabietic Acids

BY ELMER E. FLECK AND SAMUEL PALKIN

The pyroabietic acids[1] have been known for some time as highly stable conversion products of pine resin and rosin acids. Although the experimental data available on the structure of these acids are rather meager, these acids have, up to the present time, been universally regarded as isomeric with abietic and other resinic acids.

Thus assuming two double bonds, Greth[1c] believes that the difference in reactivity between abietic and pyroabietic acids can be explained on the basis of the relative position of the bonds, and proposes for the less reactive pyroabietic acid, structure I, in which he assumes that one of the bonds is common to two rings (B and C), whereas for abietic acid, he assumes structure II, the earlier form proposed by Ruzicka.[2a] Recently Fieser and Campbell[3] have obtained substantial evidence in support of structure III. Sandermann[4] also has proposed the latter structure as one of two possibilities, while Ruzicka and Bacon[2b] have proposed a structure involving distribution of the bonds between the two rings B and C, but with the position of one of the bonds (in ring C) uncertain.

As will be shown later, inferences heretofore regarding the degree of unsaturation and the assumed isomeric character of pyroabietic acid

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[1] (a) Dupont-Dubourg, *Bull. inst. pin.*, 181 (1928); (b) Fanica, *ibid.*, 155, 181 (1933); (c) Greth, *Z. angew. Chem.*, **47**, 827 (1934).

[2] (a) Ruzicka, DeGraaf and Muller, *Helv. Chim. Acta*, **15**, 1300 (1932); (b) Ruzicka and Bacon, *ibid.*, **20**, 1542 (1937).

[3] Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938).

[4] Sandermann, *Bull. inst. pin*, **30**, 138 (1937).