[CONTRIBUTION NO. 169 FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Volatile Oil and Resin of Cynomarathrum Nuttallii

BY E. K. NELSON

Cynomarathrum nuttallii A. Gray is an umbelliferous plant occurring from the Plains to the spruce belt in western Nebraska, Wyoming, Utah and northwestern New Mexico. It is also known under the name *Peucedanum graveolens*, Watson.

The roots of several species of Peucedanum formed one of the most valuable medicines among the Gosiute Indians, being, in fact, termed by them "pi-a-na-tsu," or "great medicine." In sore throats it was mashed and applied directly to the affected surface.[1]

The roots of the plant have a strong and rather pleasant aromatic odor, and therefore an investigation has been made of the volatile oil and alcohol-soluble constituents.

Material for the investigation was collected in Utah.[2] On steam distillation the ground root afforded 6% of volatile oil. Extraction of the residual material with alcohol yielded about 15% of a red balsamic or resinous material.

Examination of the Volatile Oil

The volatile oil of the roots has an odor resembling turpentine, but milder and more pleasant: d_{20}^{20} 0.869, α_D +22.6°. Sixty cc. was distilled at 6 mm.; 57 cc. boiled under 48°; and 3 cc. distilled at 90–105°. The terpene fraction, after being rectified over sodium, distilled at 164–166° at atmospheric pressure: d_{20}^{20} 0.8654, n_D^{20} 1.4739, $[\alpha]_D$ +28.59°. When oxidized with potassium permanganate and sodium hydroxide, it gave a difficultly soluble sodium salt. The acid isolated melted at 127–127.5° (corr.). 0.3219 g. of the acid in 10 cc. of ether in a 100-mm. tube had an optical rotation of +0.55°, $[\alpha]_D$ +17.08°

Admixture with nopinic acid from *l*-β-pinene caused a 10° depression in m. p., but optical crystallographic examinations[3] afforded data the same as those for *l*-nopinic acid.

The acid crystallized in colorless rods and plates. The refractive indices were: α = 1.520 (crosswise) and γ = 1.540 (lengthwise and occurring frequently); both ±0.003. The β value was not determined but was found to be very close to the γ value and shown crosswise on rods. In parallel polarized light the extinction was parallel and the sign of elongation +. The birefringence was rather strong, $\gamma - \alpha$ = 0.020; usually first order white, occasionally brilliant colors of second order were shown. In convergent polarized light, occasional partial biaxial interference figures were evident, showing that 2E was around 70°, and the sign apparently −.

Therefore the volatile oil of *Cynomarathrum nuttallii* contains about 95% of *d*-β-pinene. This form of β-pinene has been reported but once from a natural source. Rutowski and Winogradowa[4] found about 30% of *d*-β-pinene associated with α-pinene and limonene in the oil of *Ferula galbaniflua* (Boiss and Buhse).

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(1) Chamberlin, *Proc. Acad. Sci., Philadelphia*, **63**, 24 (1911).

(2) This investigation was made on material submitted to E. Yanovsky of this Bureau, by R. H. Rutledge, Ernest Winkler and Chas. De Moisy, Jr., of the U. S. Forest Service.

(3) Made by G. L. Keenan, U. S. Food and Drug Administration.

(4) Rutowski and Winogradowa, *J. prakt. Chem.*, [2] **120**, 41 (1928).

The small amount of higher boiling oil was not thoroughly examined. The last runnings crystallized in the condenser and appeared to be the same as the sesquiterpene alcohol obtained on distilling the saponified balsam with steam. The odor of the heavy oil suggested the presence of geraniol.

Examination of the Balsam

Fifty grams of the balsam, as extracted with alcohol, was treated with cold potassium hydroxide solution: 7 g., or 14%, dissolved and when acid was added to its alkaline solution was recovered as a red resinous substance.

The balsam insoluble in cold alkali was distilled with steam. A very little volatile oil was obtained from it, and this did not crystallize in the cold. Excess potassium hydroxide was then added, and the steam distillation was continued. A small amount, less than 1 g., of a solid crystalline substance then came over. It melted at 74–76° (corr.).

Anal.[5] Subs. 3.617, 4.167 mg.; CO_2, 10.082, 11.644; H_2O, 3.665, 4.273; C, 76.02, 76.21; H, 11.34, 11.47. Benzene 6.786 g., subs., 0.2827 g., Δ 0.92°, mol. wt. 222. Calcd. for $C_{16}H_{28}O_2$: C, 76.12; H, 11.19; mol. wt., 252.

When the substance was acetylated by refluxing with acetic anhydride and anhydrous sodium acetate, a deep-seated change took place. The substance could not be recovered in its original form from the reaction product. Instead, it was converted into an oil with an odor resembling that of the original balsam. Tests for a methoxyl group gave a negative result.

The alkaline solution remaining in the distilling flask was then acidified with sulfuric acid, and the distillation with steam was continued. An acid distillate was obtained, which was neutralized with sodium hydroxide and evaporated on the steam-bath to a small volume. When acidified an oily layer separated which had a distinct odor of valeric acid. The oily acid was extracted with ether. On evaporating the ether and placing the extract in the ice chest, a crystalline acid separated. This was recrystallized from ethyl acetate. It melted at 45–45.5°, and was found to be an unsaturated acid with a neutralizing equivalent of 100.12. It is therefore angelic acid. The amount recovered was small. The liquid acid, absorbed in the porous plate, was recovered, neutralized and fractionally precipitated with silver nitrate. Silver determinations on the various fractions gave 51.75, 52.44, 52.51, 52.47, 52.27 and 54.42% Ag. Calculated for silver angelate, Ag, 52.12% and for silver valerate, Ag, 51.62%.

It is therefore probable that the angelic acid is accompanied by small amounts of valeric acid and an acid or acids of lower molecular weight.

The resin left after removal of the volatile alcohols and acids was brown and brittle, and was partly soluble in sodium carbonate solution. The non-acid resins were extracted by ether from the sodium carbonate solution, and when the alkaline solution was acidified the acid resins were precipitated in a colloidal condition, but became granular on boiling. The acid resin melted at a high temperature. One gram required 2.1 cc. of $N/2$ sodium hydroxide in the cold and 3.25 cc. of $N/2$ sodium hydroxide when boiled with an excess of the alkali, indicating the presence of lactones or anhydrides. The neutralizing equivalent calculated from the last titration equals 615.

Summary

The root oil of *Cynomarathrum nuttallii* was found to consist mainly (about 95%) of *d*-β-pinene. The balsam extracted from the root by alcohol is a mixture of neutral and acid resins.

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(5) Microanalysis was made by Joseph R. Spies, Insecticide Division, Bureau of Chemistry and Soils.

Angelic acid and a crystalline substance, which is probably an unstable sesquiterpene alcohol, were recovered from the saponification products of the balsam. Both are minor constituents.

WASHINGTON, D. C.
RECEIVED APRIL 6, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride. V. The Rearrangement of Isopropylphenol, *o*-, *m*- and *p*-Cresyl Ethers

BY F. J. SOWA,[1] H. D. HINTON AND J. A. NIEUWLAND

In a previous publication[2] it was shown that the rearrangement of alkyl phenyl ethers could be accomplished by the use of boron fluoride as the rearranging agent and that the position occupied by the migrating group was similar to that of an earlier report.[3]

Later,[4] a procedure was outlined by which propylene could be condensed with phenol, using boron fluoride as a catalyst. It was noted, during the rearrangement of alkyl phenyl ethers, that if the reaction were allowed to take place spontaneously or if the temperature were raised considerably during the reflux process, in the presence of boron fluoride, several higher boiling fractions other than the first rearranged products were isolated. This investigation has been a study of the rearrangement of isopropyl phenyl and cresyl ethers under the conditions just mentioned. The experimental work gives some information that deals directly with the course of condensation and rearrangement of alkyl aryl ethers using boron fluoride as the agent.

Huston and his collaborators[5] investigated the action of benzyl alcohol on *o*-, *m*- and *p*-cresol in the presence of aluminum chloride. They obtained monobenzyl and dibenzyl cresols. Niederl and Natelson[3,6] studied the rearrangement of saturated alkyl phenyl and cresyl ethers but they did not report the isolation of any phenols other than the mono-substituted isopropylphenol or cresols.

If boron fluoride is passed into isopropyl phenyl ether without cooling, the mixture becomes quite warm and then a violent reaction takes place. Among the products of the reaction from 250 g. of the ether are: the phenols, phenol (90 g.), 2-isopropylphenol (34 g.), 2,4-diisopropylphenol

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[1] From the third part of the Dissertation presented by Frank J. Sowa to the Committee on Graduate Study of the University of Notre Dame in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1933.

[2] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

[3] Niederl and Natelson, *ibid.*, **53**, 1928 (1931).

[4] Sowa, Hinton and Nieuwland, *ibid.*, **54**, 3694 (1932).

[5] Huston, *ibid.*, **52**, 4484 (1930); *ibid.*, **53**, 2379 (1931); *ibid.*, **54**, 1506 (1932).

[6] Niederl and Natelson, *ibid.*, **54**, 1063 (1932).