one per cent of its body weight of food within 15 to 20 minutes. If the minimum lethal dose of red-squill powder is 1000 milligrams per kilogram and a bait is prepared containing 10 per cent of squill, the consumption of 1 per cent of its body weight will cause death. In case the lethal dose is less than 1000 milligrams per kilogram, a corresponding decrease in squill content may be made. It is suggested that squill baits be prepared and used at this uniform toxicity. Tests have shown that wild rats and white rats show practically identical sensitivity to squill. The average weight of the wild rats used in this investigation was 30 grams (10 ounces). Such a rat would require 3 grains, or $^1/_{10}$ ounce, of this standard squill bait. In these investigations rats were found to eat several times this quantity of food.

Cats, dogs, chickens, pigeons, pigs, woodchucks, prairie dogs and pocket-gophers refused to eat baits containing 10 per cent of squill powder (100,000 parts per million). Many cats refused to eat lean hashed meat containing 10 to 25 parts of squill powder per million, or consumed this food very slowly. When administered in gelatin capsules or by stomach tube, prompt and thorough emesis was produced. No other effect was noted. From these feeding and stomach-tube experiments, it was concluded that baits containing 5 to 10 per cent of squill powder either will not be eaten by animals other than rats or will produce emesis with direct removal of the bait.

CONCLUSIONS.

(1) A method of producing uniformly toxic red-squill powders has been developed.

(2) The usual lethal dose of these powders is approximately 250 milligrams per kilogram when fed to white or wild rats.

(3) No serious injury to pigs, cats, dogs, chickens, pigeons or other domestic animals should be anticipated when red-squill baits are exposed to kill rats.

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THE LEAF OILS OF WASHINGTON CONIFERS: I. INTRODUCTION.*

BY ARNOLD J. LEHMAN AND E. V. LYNN.

Very few volatile oils from the leaves of conifers growing in the state of Washington have been examined completely. Of oils from the twenty or more species, five have been studied more or less thoroughly but, in order to give us complete knowledge of the composition, much more work needs to be done. Four other oils have been prepared and their common constants determined, although little is known of the constituents. No attempt has been made to prepare oils from the other species, which present, therefore, a virgin field for the phytochemist.

It seemed desirable and interesting to prepare and investigate all of these oils in a systematic manner. The use in industry and medicine of various "pine oils" is well known. Some of these are known to possess peculiar properties which fit them for the applications made, but in most of them the composition, properties

* Scientific Section, A. PH. A., Rapid City meeting, 1929. No discussion.

or even source is unknown. Furthermore, many of the coniferous trees might furnish oils which would be of much greater value were they examined carefully.

As a start in this direction, the logical procedure would be to prepare the products and determine their composition. It was with such an idea in mind that the present series was started. It is strictly confined to the "pines" of Washington. In this paper we propose to present in abstract the chemical and physical work which has already been done; subsequently we will report our work on each species.

The following list, adapted from Piper, "The Flora of Washington," gives the coniferous species growing in the state.

Taxus brevifolia
Juniperus communis sibirica
Juniperus occidentalis
Juniperus scopulorum
Chamaecyparis nootkatensis
Thuja plicata
Pinus monticola
Pinus albicaulis
Pinus ponderosa
Pinus contorta
Larix lyallii
Larix occidentalis
Abies nobilis
Abies lasiocarpa
Abies amabillis
Abies grandis
Pseudotsuga mucronata
Tsuga mortensiana
Tsuga heterophylla
Picea sitchensis
Picea engelmanni

The oils from eight of them have been prepared and more or less completely examined.

JUNIPERUS COMMUNIS.

In spite of the fact that an oil from the fruit is described by the U. S. P. and that products from the wood have been frequently studied, little is known of that from the leaves. Hansen and Babcock (3) obtained 0.15 to 0.18 per cent of an oil having a yellow color, a juniper odor, and a specific gravity of 0.8531. Pigulevski (17) received 0.44 to 0.58 per cent of oil having the following constants: $d_{15.6}$ 0.9258; saponification number 55.33; acid value 10.71. Southall (11) obtained a product from the whole shrub which contained no aldehydes, phenols or ketones. It had d 0.854, $[\alpha]_D$ −1.00°, n_D 1.4711, acid value 0.19, ester value 1.15, and acetyl value 14.19. Apparently no one has yet identified any constituents.

CHAMAECYPARIS NOOTKATENSIS.

The oil from this species has been examined but once. Clark and Lucas (18) found that the air-dried leaves yielded 0.7 to 2.0 per cent of oil with a specific gravity of 0.855 to 0.888 and an index of refraction of 1.472 to 1.474. Although the boiling point ranged from 155° to 280° C., the only constituents identified were limonene, alpha pinene and cymene, with the probability that beta pinene and sabinene are also present.

THUJA PLICATA.

The leaves of this common Washington cedar furnish a volatile oil which has been investigated several times. Blasdale (2), in 1907, reported the constants as follows: $d_{15°}$ 0.8997; n_D 1.4575; $[\alpha]_D$ + 1° 45′; boiling point 150–225° C. Most of it distilled at 198–200° C. and contained thujone.

Two years later Brandel and Dewey (4) recorded the results of a rather ex-

tended investigation of the oil, which they obtained in 0.8 to 1.4 per cent yield. It had a bright yellow color and a camphoraceous odor, $d_{25°}$ 0.9305, $[\alpha]_D^{25°}$ −6.9°, acid number 0.5, saponification value 5.7, and acetylization number 6.2, corresponding to 28.5 per cent of alcohols. Alpha pinene was present to the extent of about 3 per cent, but the main body consisted of thujone, fenchone and borneol esters. A remarkable fact brought to light was that, whereas the whole oil was laevorotatory, all fractions were dextro.

The French variety yielded 1.32 per cent of oil (5) containing thujone. It had a specific gravity of 0.9056 at 15° C., a specific rotation of +5° 4′, an index of refraction of 1.45721, an acid value of 0.8 and an ester value of 16.9.

Rose and Livingstone (9) obtained about 1 per cent of oil, specific gravity 0.913 at 20° C., specific rotation −4.77° at 20° C., index of refraction 1.4552, acid value 0.5, ester number 2.28, acetyl number 8.8. They found 80–85 per cent of thujone, 3–5 per cent of pinene, 1–3 per cent of tanacetyl alcohol and 1–2 per cent of its acetic ester.

PINUS PONDEROSA.

In 1879 Sadtler (1) described the separation and some of the properties of a liquid, abietine, from the oil of this species. Schimmel & Co. (7) made a report on a "yellow pine oil" of commerce, but they think this was probably derived from P. palustris.

Schorger (12), in 1914, made an extensive study of oils from the leaves and twigs and also from the cones. The former was found to contain about 75 per cent of beta pinene, 7 per cent of borneol, 6 per cent of dipentene, 2 per cent of alpha pinene, 2 per cent of bornyl acetate and 3 per cent of "green oil." Miller and Lynn (14) confirmed the presence of the pinenes.

PINUS CONTORTA.

The oil from leaves and twigs of *Pinus contorta* has been examined only by Schorger (13), who reported a specific gravity of 0.8690, index of refraction 1.4831, specific rotation −17.84°, acid value 0.9, ester value 6.02, acetyl value 32.39. The yield obtained amounted to 0.234 per cent. He found present 49–50 per cent of beta pinene, 7.5 per cent of borneol, 5–6 per cent of camphene, 3 per cent of alpha pinene, 7 per cent of cadinene and 2 per cent of bornyl acetate. A trace of furfural was noted in the first distillate and the presence of methyl chavicol was suspected.

PSEUDOTSUGA MUCRONATA.

The leaves and twigs of the common Douglas fir furnish an oil which has been studied by several observers. Sweet (6) received 0.8 to 1.0 per cent of a greenish yellow oil having a lemon-like odor. This had a specific gravity of 0.8680 at 23° C., a specific rotation of −62.5°, saponification value 86.6 equivalent to 30.3 per cent of bornyl acetate, acetyl value 91.2 equivalent to 23.3 per cent of borneol. The chief terpene was camphene, and borneol was also present, but no aldehydes or free acid.

Schorger (10) obtained an average yield of 0.16 per cent of an oil with the following constants: d 0.8727–0.8759; $[\alpha]_D$ −17.02–22.17°; n_D 1.4758–1.4780; acid value 0.65–1.1; ester value 11.1–24.2. He found alpha pinene 25 per cent, beta pinene 48 per cent, limonene 6 per cent; borneol 6.5 per cent and a green oil

distilling at 125-205° C. under a pressure of 20 mm., which apparently consisted of sesquiterpenes. A trace of furfural was noted in the first runnings, but no camphene was to be detected.

Bennett (15) found that old trees growing in England gave more than ten times as much oil as young ones, his yield varying from 0.01 to 0.11 per cent. He reported specific gravity 0.876 and 0.905, index of refraction 1.4835 and 1.4717, rotation −7° and −46°, ester numbers corresponding to 21.4 and 34.5 per cent of bornyl acetate. Geraniol was separated but not entirely identified, as were also limonene, citral and alpha pinene.

TSUGA HETEROPHYLLA.

Cable (16) examined three samples of the Western hemlock oil collected at various times of the year. He obtained the following figures: yield 0.32 to 0.36 per cent; d_{15}^{20} 0.844 to 0.852; $[\alpha]_D$ −6.74 to −20°; n_D 1.4790 to 1.4840; acid value 2.5 to 3.4; ester value 6.7 to 17.0, equivalent to 2.3 to 6.0 per cent of bornyl acetate; ester value after acetylization 19.6 to 33.4, equivalent to 5.4 to 9.2 per cent of total borneol. None of the constituents were identified.

PICEA ENGELMANNI.

This species has been investigated only by Swenholt (8) who obtained 15 cc. of oil. The specific gravity was 0.895, the rotation was +1° 53′, and the saponification number was 24.15 corresponding to 8.5 per cent of ester as bornyl acetate. The oil had a strong camphoraceous odor.

From the foregoing review, it will be readily apparent that but a comparatively few species have received more than superficial attention. It would undoubtedly be of great interest to examine all of the others. It is true that the majority which have already been studied possess a certain similarity of composition, but our work to date has indicated a greater difference than is generally presumed. We have already nearly completed the investigation of four other species and expect to report on them shortly.

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