

THE CHEMICAL EXAMINATION OF ESSENTIAL OILS FROM *ABIES AMABILIS* AND *GRANDIS*.*BY MALCOLM S. TRUPP¹ AND LOUIS FISCHER.²

PART I.

Abies amabilis (Forbes), commonly known as "white fir" or "silver fir," is a coniferous tree growing abundantly in dense forests on the western slopes of the Cascade Mountains, preferably on benches or flats or on the lower slopes of canyons where excellent soil drainage is available and at altitudes ranging from 1000 to 6000 feet above sea level. This tree attains a height of from 100 to 150 feet and varies between 3 and 5 feet in diameter.

A superficial study of the volatile oil from the bark of *Abies amabilis* was conducted by Rabak (1), who determined a few physical constants and stated that the oil contained lævo-pinene and probably lævo-limonene.

EXPERIMENTAL.

Two lots of bark, collected in December 1936 in the vicinity of Mt. Rainier National Park, Washington, were subjected to steam distillation. From a total of 316 pounds of fresh bark there were obtained 850 cc. or 1.60 pounds of oil which represented a yield of 0.50 per cent. The dry oil, faintly yellow in color, possessed a slight aromatic odor.

The physical constants, determined in the usual manner, were as follows: d_{20} 0.8576; n_D^{20} 1.4772; $[\alpha]_D^{20}$ -10.52°; saponification number 2.22; acid number 0.26; ester number 1.96; and acetyl number 6.18.

Free Acids: Acetic Acid.—Five hundred cubic centimeters of the oil were extracted with 5 per cent sodium carbonate solution. The basic solution, upon acidification and extraction with ether, furnished 0.075 Gm. of acidic material, representing a yield of 0.017 per cent. This material, after mixing with hot water, was filtered. The filtrate, neutralized with calcium hydroxide and evaporated to dryness, was extracted with alcohol. The residue, remaining, gave the usual tests for acetic acid. Although traces of acidic materials insoluble in hot water were left on the filter, insufficient evidence was obtained for their identification.

Phenols.—Extraction of the oil with 5 per cent potassium hydroxide solution and subsequent treatment of the acidified liquid with ether yielded 0.035 Gm. of oily residue, representing 0.008 per cent of the oil by weight. A solution of this material in alcohol produced a purple color with ferric chloride solution. No identification was possible, since several phenols give similar color reactions.

Aldehydes.—Because the oil gave reduction tests with Tollen's and Schiff's reagents, it was extracted with a saturated solution of sodium bisulfite. This solution, decomposed with sodium carbonate and extracted with ether, yielded a negligible quantity of oily substance. Extremely small traces of aldehyde materials were present, although no satisfactory identifications could be made.

Fractionation.—The remaining oil, free from acids, phenols and aldehydes was dried, filtered and subjected to fractional distillation. The liquid, boiling below 100° C. at reduced pressure, was fractionated repeatedly until the following fractions were obtained:

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² This paper was directed jointly by Louis Fischer, College of Pharmacy, University of Washington, and Russell A. Cain, Sharp and Dohme Laboratories.

Fraction No.	Boiling Point, ° C.	Volume, Cc.	Per Cent by Volume.	$[\alpha]_D^{20}$.	n_D^{20} .	n_D^{20} .
I	157-162	19.0	3.80	-13.48°	0.8993	1.4898
II	163-173	339.0	67.80	-11.48°	0.8597	1.4891
III	174-178	2.2	0.44
IV	178-208	2.0	0.40

Levo-Alpha-Pinene.—A nitrosochloride was prepared from Fraction I according to the method of Wallach (2). This derivative, purified by precipitation from a chloroform solution with methyl alcohol, was found to melt at 109° C. Admixture with a nitrosochloride prepared from turpentine oil caused no reduction in the melting point.

For further confirmation of this constituent, five cc. of this fraction were oxidized to pinonic acid with concentrated potassium permanganate solution following the method of Parry (3). A semicarbazone prepared from the pinonic acid after recrystallization from hot alcohol melted at 204° C. The results obtained indicate the above fraction to be composed principally of alpha-pinene. The above derivatives were also obtained from Fraction II, indicating the presence of appreciable quantities of alpha-pinene.

Levo-Beta-Pinene.—A portion of Fraction II was oxidized to sodium nopinate with concentrated permanganate solution in the presence of sodium hydroxide, according to the method of Wallach (4). An acidified solution of sodium nopinate was extracted with ether. The nopinic acid, after crystallization from the solvent, melted at 124-125° C. Since only small quantities of nopinic acid were obtainable and the preparation of other derivatives was dependent upon this substance, one may conclude that limited amounts of beta-pinene are present in Fraction II as indicated by the above results.

Levo-Beta-Phellandrene.—A solid nitrite was prepared from Fraction II using the method of Wallach and Gildemeister (5). After purification by precipitation from a cooled acetone solution with water, this derivative was found to melt at 98° C. This corresponds to the melting point of beta-phellandrene-beta-nitrite.

For further identification a cooled portion of the above fraction was oxidized with potassium permanganate solution according to Wallach's method (6). After removal of unoxidized materials from the concentrated aqueous solution, a glycol was extracted with chloroform. This substance, upon dehydration with 50 per cent sulfuric acid and subsequent steam distillation, furnished tetrahydrocuminic aldehyde. A semicarbazone, prepared from the latter and precipitated from acetone, melted at 202° C. The above derivatives indicated the presence of appreciable amounts of beta-phellandrene in Fraction II. In a similar manner, beta-phellandrene was also found to be present in Fraction IV.

Combined Acids: Acetic Acid.—The oil distilling above 100° C. at reduced pressure was saponified with alcoholic potassium hydroxide. After removal of the alcohol, the aqueous washings were acidified and extracted with ether. A total of 0.883 Gm., representing a yield of 0.21 per cent of acidic material, was obtained. The aqueous distillate of this mixture, after steam distillation, was neutralized with calcium hydroxide solution, evaporated to dryness and extracted with alcohol. The usual qualitative tests were obtained for acetic acid. No non-volatile acids could be identified although they represented the greater portion of the acid residue.

Fractionation of the High-Boiling Portion.—The oily portion, freed of combined acids, represented 2.55 per cent of the original volume. After several refractionations at reduced pressure the following fractions were obtained:

Fraction No.	Boiling Point (24 mm.), ° C.	Volume, Cc.	Per Cent by Volume.	Color.
I	110-114	1.0	0.20	Colorless
II	150-157	1.0	0.20	Yellow
III	184-208	2.0	0.40	Orange
	Residue	Brown

Although Fractions I and II were thought to contain alcohols, none could be identified. No constituents could be identified in Fraction III which was slightly decomposed.

SUMMARY.

The fresh bark yielded 0.50 per cent of essential oil, containing 72.4 per cent of terpenes and 2.55 per cent of high boiling liquid. The terpenes present were mainly lævo-alpha-pinene and lævo-beta-phellandrene with smaller quantities of lævo-beta-pinene. Traces of free acetic acids, phenols and aldehydes were present. Only acetic acid could be identified in the combined state although some non-volatile acids were undoubtedly present.

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PART II.

In the above it was stated that the oil from the bark of *Abies amabilis* (Forbes) had been superficially examined. However, a complete survey of the literature revealed that, up to the present time, no attempts had been made to investigate the oil from the leaves of this tree.

EXPERIMENTAL.

The small twigs with leaves attached, collected between November 1936 and December 1937 from trees located in the vicinity of Mt. Rainier National Park, Washington, were distilled with steam. A total of 889.75 pounds of fresh leaves and twigs yielded 0.713 pound of volatile oil, corresponding to 0.08 per cent. The oil was colorless and possessed an odor similar to that of turpentine oil.

The physical and chemical constants, determined in the usual manner, were as follows: $[\alpha]_D^{20}$ -3.79° ; d_{20} 0.8574; n_D^{20} 1.4770; saponification number 4.63; acid number 0.80; ester number 3.83; and acetyl number 12.29.

Free Acids.—The free acids, removed from 351 cc. of the oil with 5 per cent sodium carbonate solution, were liberated by the addition of acid to the alkaline liquid and extracted with ether. A total of 0.06 Gm. of brown, syrupy, acidic residue was obtained, representing 0.02 per cent of the original oil by weight. A portion of the residue, neutralized with calcium hydroxide, produced an ester-like odor in the presence of ethyl alcohol and sulfuric acid. However, after the application of the usual methods of analysis no individual acids could be identified.

Phenols.—The phenolic substances, extracted from the oil with 5 per cent potassium hydroxide solution, were liberated from the alkaline solution by acidification with sulfuric acid and extracted with ether. A small amount of viscous material, possessing a tarry odor, was obtained weighing 0.0995 Gm. and representing a yield of 0.03 per cent. A portion of this substance in aqueous solution produced a purple color with ferric chloride and in alcoholic solution a reddish brown color, indicating the presence of phenols. Since these color reactions are common to several phenols no identification was possible.

Aldehydes.—Because the oil slowly reduced Tollen's reagent and restored the color to Schiff's reagent, the aldehydes were removed from it by shaking with a saturated solution of sodium bisulfite. This solution was then decomposed with a warm, saturated solution of sodium carbonate and extracted with ether. Upon recovery of the ether, a small quantity of oily residue remained, weighing 0.0503 Gm. and representing a yield of 0.02 per cent. A semicarbazone was formed with this material but it was insufficient in quantity to perform a melting point determination.

Fractionation.—A total of 330 cc. of the dried oil, free from acids, phenols and aldehydes, was separated into a low- and high-boiling portion by several distillations. The low-boiling liquid, distilling from 60–66° C. at about 14 millimeters, was repeatedly refractionated at reduced and atmospheric pressure until the following fractions were obtained:

Fraction No.	Boiling Point (763.8 mm.), ° C.	Volume, Cc.	Per Cent by Volume.	d_{40} .	$[\alpha]_D^{20}$.	n_D^{20} .
I	161–167	127.0	38.48	0.8562	–2.04°	1.4735
II	167–171	124.0	37.57	0.8532	–3.07°	1.4761
III	173–186	10.0	3.03	0.8580	–9.90°	1.4804
	Residue	7.0	2.12

Lavo-Alpha-Pinene.—A nitrosochloride, prepared according to the method of Ehestädt (1) from the fraction distilling between 161–167° C., was purified by precipitation from a cooled chloroform solution with methyl alcohol. This derivative melted at 110° C. Depending on the purity of this compound, considerable variation (103–115° C.) in the melting points have been observed (2).

The more stable nitrolbenzylamine derivative was prepared from the nitrosochloride by Wallach's method (3). The dry crystals, which had been precipitated from water and washed with alcohol, were found to melt at 122–123° C., the true melting point for the pure substance.

To further prove the presence of alpha-pinene, a portion of the above fraction was oxidized to pinonic acid with potassium permanganate, following the method of Parry (4). The semicarbazone of the acid was prepared and, after recrystallization from hot alcohol, melted at 204.5° C. The results show the above fraction to consist chiefly of alpha-pinene. Alpha-pinene was found to be present in Fraction II by similar oxidation methods.

Lavo-Beta-Pinene.—A portion of Fraction I yielded nopinic acid when oxidized with an alkaline solution of potassium permanganate using Wallach's method (5). The acid after recrystallization from an ether-benzene solution melted at 124–125° C. Since this melting point was near that of the pure compound, it was assumed that small amounts of beta-pinene were present in Fraction I.

Lavo-Beta-Phellandrene.—A solid nitrite was prepared from a portion of Fraction III according to the method of Wallach and Gildemeister (6). This derivative, after purification by recrystallization from a cooled aqueous acetone solution, melted at 102.5° C. corresponding to the pure compound.

For further identification, a nitrosochloride was prepared from a portion of the fraction according to the method of Ehestädt (1). This substance, when purified by precipitation from a chloroform solution with methyl alcohol, melted at 108° C. Although this melting point does not agree exactly with that of the pure compound, the results point to the possible presence of small quantities of beta-phellandrene in this fraction.

SAPONIFICATION AND DISTILLATION OF THE HIGH-BOILING LIQUID.

The high-boiling liquid after saponification was washed free of salts and excess alkali, dried and fractionally distilled at reduced pressure. The following portions were obtained after repeated refractionations:

Fraction No.	Boiling Point (14 mm.), ° C.	Volume, Cc.	Per Cent by Volume.	d_{40} .	$[\alpha]_D^{20}$.	n_D^{20} .
I	71–90	9.3	2.81	0.8621	–5.41°*	1.4812
II	90–110	2.0	0.60	0.8903	–7.64°	1.4872
III	110–130	2.1	0.63	0.9077	–6.16°	1.4890
IV	130–147	4.7	1.42	0.9101	1.45°	1.4949
	Residue

* In chloroform.

Although either phellandrene or terpinene was suspected in Fraction I, no solid derivatives could be prepared for identification.

All efforts to identify sesquiterpenes or alcohols in Fractions II and III proved to be negative, neither could any trace of sesquiterpenes be distinguished in the fourth fraction.

Combined Acids: Acetic Acid.—After saponification of the high-boiling liquid, the alkaline washings were acidified with dilute sulfuric acid and steam-distilled. The aqueous distillate containing no insoluble volatile material was neutralized with calcium hydroxide solution, evaporated to dryness and extracted with alcohol. The residue remaining gave the usual tests for acetic acid. Only traces of other volatile acids seemed to be present.

Upon removal of the solvent, from an ether extract of the liquid remaining in the distillation flask, a brown residue was obtained. Neutralized portions of this residue formed insoluble salts with silver nitrate, but the silver content of each portion varied too greatly for accurate identification.

SUMMARY.

The fresh leaves and twigs of *Abies amabilis* yielded 0.08 per cent of volatile oil which contained traces of free acids, phenols and aldehydes. The low-boiling portion consisted of 81.21 per cent of terpenes; alpha-pinene being present in the largest quantities with smaller amounts of beta-pinene and beta-phellandrene. No sesquiterpenes or alcohols could be identified in the high-boiling liquid which represented 12.42 per cent of the original oil. Acetic acid was found to be the principal combined acid.

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PART III.

Abies grandis (Lindley), commonly known as the grand or white fir, is a tall, straight tree growing to a height of from 150 to 275 feet and is 3 to 4 feet in diameter. It may be found growing from sea level to an altitude of 3000 feet or more, usually preferring low benches or flats where excellent soil drainage is available.

The volatile oil from the leaves and twigs of this tree was recently investigated by Charles Schwartz, Jr. (1), who determined the physical constants of the oil and found it to contain the terpenes alpha-pinene, beta-pinene, beta-phellandrene and camphene. Analysis also indicated the presence of borneol, as bornyl acetate, and traces of free acids and phenols.

The volatile oil, obtained from the bark of *Abies grandis*, has not been previously examined.

EXPERIMENTAL.

The bark from the white fir was collected in May 1937 from trees growing in the vicinity of Enumclaw, Washington. The fresh bark weighing 576 pounds was steam-distilled and produced 981.95 Gm. of oil which represented a yield of 0.37 per cent.

The physical and chemical constants were determined in the usual manner and were as follows: $[\alpha]_D^{20}$ -32.83° ; d_{20} 0.8935; n_D^{20} 1.4917; saponification number 54.57; acid number 0.39; ester number 54.18; and acetyl number 8.85; total esters (calculated as bornyl acetate) 18.90; total alcohols (calculated as borneol) 18.01; combined alcohols (calculated as borneol) 14.83; and free alcohols (calculated as borneol) 3.18.

Free Acids.—Extraction of 500 cc. of the oil with a 5 per cent sodium carbonate solution and subsequent treatment of the acidified aqueous solution with ether yielded 0.2675 Gm. of yellow residue, which represented 0.05 per cent of the oil. The residue was distilled with steam, the distillate neutralized with calcium hydroxide, evaporated to dryness and extracted with alcohol. The residual material was found to contain acetic acid upon application of the usual qualitative tests. Although small amounts of the other lower fatty acids possibly were present none could be identified.

Phenols.—The oil was then treated with a 5 per cent potassium hydroxide solution, acidified and extracted with ether. A yield of 0.0943 Gm. of phenolic materials representing 0.02 per cent, was obtained. The residue was a viscous, reddish brown liquid and possessed a faint musty-like odor. An aqueous solution of this substance gave a purple color with ferric chloride indicating the presence of phenols. Another portion of the residue with phenylisocyanate produced a phenylurethane, which melted at 49–50° C. A review of the known phenylurethanes gave no clue to the identity of this material and insufficient substance was at hand for further investigation.

Aldehydes.—Since the oil slowly reduced Tollen's and Schiff's reagents, it was extracted with a saturated solution of sodium bisulfite. The latter solution was then decomposed with dilute sulfuric acid and extracted with ether. The oily residue so obtained was too small for further investigation.

Fractionation.—Four hundred and sixty-eight cubic centimeters of oil, free from acids, phenols and aldehydes, were separated into a low- and high-boiling portion by fractional distillation at reduced pressure. After repeated refractionations of the low-boiling liquid at reduced and finally at atmospheric pressure, the following fractions were obtained:

Fraction No.	Boiling Point (748.6 mm.), ° C.	Volume, Cc.	Per Cent by Volume.	$[\alpha]_D^{20}$.	d_{20} .	n_D^{20} .
I	159–162	92.0	19.65	–39.40°	0.8692	1.4847
II	162–165	89.0	19.44	–32.77°	0.8729	1.4887
III	165–172	72.0	15.38	–33.05°	0.8637	1.4896
IV	172–179	18.0	3.84	–32.49°	0.8820	1.4910
V	185–205	7.0	1.49	0.9248	1.4856

Levo-Alpha-Pinene.—A solid chlorohydrate derivative was obtained when dry hydrogen chloride gas was passed through a cooled portion of Fraction I. After several recrystallizations from alcohol, the derivative was dried and found to melt at 124–125° C.

For further identification, another portion of this fraction was oxidized to pinonic acid with concentrated potassium permanganate solution using the method of Parry (2). A semicarbazone derivative, prepared from the pinonic acid, was purified by recrystallization from hot alcohol and after drying melted at 204–205° C. The derivatives, formed, prove the main constituent of Fraction I to be alpha-pinene.

Levo-Beta-Pinene.—A portion of Fraction II was examined for beta-pinene by oxidation with potassium permanganate in the presence of sodium hydroxide according to the method of Wallach (3). The principal oxidation product, sodium nopinate, was then acidified with dilute sulfuric acid and extracted with ether. Evaporation of the solvent yielded long, colorless needle-like crystals of nopinic acid which melted at 126–126.5° C. Admixture with a known nopinic acid produced no depression in the melting point.

Beta-pinene was further identified by the oxidation of the nopinic acid with one per cent potassium permanganate solution to form the ketone nopinone. A semicarbazone of nopinone, recrystallized from alcohol, was found to melt at 188–190° C. From the amounts of the derivatives prepared, one can conclude that beta-pinene is the chief component of Fraction II. In a similar manner, Fraction III was found to contain beta-pinene.

Levo Camphene.—A portion of Fraction II, boiling from 162–165° C., was hydrated to isobornyl acetate with glacial acetic acid following the method of Bertram and Walbaum (4). After saponification of the isobornyl acetate, the isborneol was precipitated by throwing the mixture into water. The isborneol was obtained in a pure state after absorption of the excess oily material on a porous plate. Recrystallized from alcohol, it melted at 208° C.

Although no phenylurethane could be formed for further identification, the results obtained would seem to indicate the presence of appreciable quantities of camphene in Fraction II.

Lævo-Beta-Phellandrene.—A solid nitrite derivative, prepared from a portion of Fraction III according to the method of Wallach and Gildemeister (5), was purified by recrystallization from a cooled, diluted acetone solution. The resulting crystals of beta-phellandrene-alpha-nitrite, after drying, melted at 104° C.

For further identification, another portion of the fraction was oxidized to a glycol with one per cent potassium permanganate solution using the method of Wallach (6). The resulting glycol, obtained by extraction from the aqueous liquid with chloroform, was steam-distilled in the presence of 50 per cent sulfuric acid. A semicarbazone of tetrahydrocuminic aldehyde was formed from the distillate and, after recrystallization from methyl alcohol, melted at 204° C.

Similar results were obtained with Fraction IV indicating that beta-phellandrene was present in each fraction.

Examination of the High-Boiling Liquid.—The high-boiling portion of the oil, measuring 158 cc. and representing a third of the original volume, was saponified with alcoholic potassium hydroxide. After the alcohol was removed by distillation, the oily material was washed free of salts, dried, filtered and subjected to fractional distillation at reduced pressure. Fraction I proved to be a camphor-like solid, and after its separation, the remainder of the liquid was repeatedly refractionated until the following fractions were obtained:

Fraction No.	Boiling Point (10 mm.), ° C.	Volume, Cc.	Per Cent by Volume.	$[\alpha]_D^{20}$.	d_{20} .	n_D^{20} .
I	104-114	Solid	-48.32°*
II	127-137	17.0	3.63	-4.79°	0.9161	1.5112
III	137-147	19.0	4.16	-1.78°	0.9231	1.5165

* In chloroform.

Lævo-Borneol.—The crystalline solid, after purification by recrystallization from alcohol, was found to melt at 203-203.5° C., corresponding favorably to the melting point of pure borneol.

For further identification, a phenylurethane, prepared in the usual manner and recrystallized from petroleum benzin, melted at 138° C. The melting point of the solid, in addition to that of the phenylurethane, was sufficient for the identification of borneol.

Lævo-Cadinene.—A portion of Fractions II and III was saturated with dry hydrochloric acid gas according to Wallach's method (7). The prepared chlorohydrate derivative was purified by recrystallization from a mixture of ether and alcohol. After drying, the crystals melted at 117-118° C. A bromohydrate derivative, prepared in a similar manner from each fraction, melted at 123-124° C.

The melting points of the above derivatives correspond to those of lævo-cadinene, which must be the chief component of these fractions.

Combined Acids: Acetic Acid.—After saponification of the high-boiling liquid, the alkaline washings were acidified with dilute sulfuric acid and extracted with ether. The residue amounted to 1.5437 Gm. and corresponded to 0.36 per cent of the original oil used for fractionation. The acid residue, entirely soluble in water, was neutralized with milk of lime, evaporated to dryness and extracted with alcohol. The material insoluble in alcohol was examined for acetic acid and identified by the usual qualitative tests. Acetic acid was undoubtedly the principal combined acid.

The residue soluble in alcohol was neutralized and precipitated with concentrated silver nitrate solution. The insoluble silver salt, after ignition, contained 51.40 per cent of silver. Silver isovalerate contains 51.65 per cent of silver. Since these results correspond so closely, it is possible that a small amount of isovaleric acid was present in the combined state.

SUMMARY.

The bark of *Abies grandis* yielded 0.37 per cent of volatile oil. The physical and chemical constants were determined in the usual manner. Traces of free acetic acid, phenols and aldehydes were present. The low-boiling liquid, representing 59.40 per cent of the oil, was composed of terpenes consisting chiefly of alpha-pinene, beta-pinene, beta-phellandrene and small amounts of camphene. The

high boiling liquid, representing 33.76 per cent of the oil, constituted mainly bornyl acetate and the sesquiterpene, lævo-cadinene.

Acetic acid was the principal combined acid with isovaleric acid possibly present in small quantities.

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THE PIGMENTS CONTAINED IN THE BARK OF THE ROOT OF CELASTRUS SCANDENS.*

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1. CELASTROL.

At one time some investigators thought that the chief pigment found in the outer bark of the root of *Celastrus scandens* was β -carotene. β -Carotene is of great importance because of its use as a standard for vitamin A, and therefore confirmation of its existence in a plant from which it might be easily isolated and purified was deemed advisable.

EXPERIMENTAL.

The material investigated was collected near Savage, Minn. The outer bark of the freshly collected roots of *Celastrus scandens* was readily removed with a vegetable grater. The bark thus obtained was ground and extracted with Skelly-solve B. The principal pigment contained in the bark was more soluble than other pigments present in lesser quantities, and therefore could be separated from them by fractional extraction. The first Skelly-solve B. extract contained so much pigment that it separated during the process of extraction. Upon prolonged extraction with fresh solvent, other pigments also separated. These varied in color from orange to yellow and some were even brown.

Celastrol.—Approximately 40 Gm. of the chief pigment were obtained as ruby-red cubes. They were recrystallized from a mixture of isopropyl ether and Skelly-solve B. The crystals melted apparently at 205° C. although there was evidence of decomposition. Additional recrystallizations failed to raise the observed melting point. Further investigations have shown that this compound contains hydroxyl groups and therefore the name celastrol is proposed. Celastrol is soluble in the fat solvents and in ethyl and methyl alcohols. It can be shaken from an ether solution with aqueous sodium hydroxide or sodium carbonate. The sodium salt forms a very dark red solution. The pigment cannot be shaken from ether by means of aqueous sodium bicarbonate. It forms a barium salt which is insoluble in methyl alcohol. Celastrol can be extracted from petroleum ether with 60 per cent or stronger aqueous methyl alcohol. The specific rotation of celastrol was very difficult to obtain because of the exceedingly dark-colored solutions.

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