

Fraction.	Amount.	n_D^{23} .	d_{25} .	$[\alpha]_D^{25}$.
155-160° C.	5.0%	1.4729	0.8501	...
160-163	4.0	1.4725	0.8530	-17.75°
163-168	22.0	1.4749	0.8575	-20.67
168-173	37.0	1.4772	0.8556	-23.50
173-177	6.0	1.4810	0.8444	-32.50
177-179	3.5	1.4812
179-203	4.0	1.4839	0.8595	...
At 45-50 mm.				
94-145	5.0	1.4825	0.8880	-34.50
145-190	2.0	1.4982	0.8942	...
190-208	2.0	1.5051	0.9389	...
208-216	6.0	1.5125	0.9389	...
Residue	3.5

melting point 124-125° C. The second and third fractions undoubtedly contained some camphene, but this could not be proved. Hydration gave the typical odor of isoborneol, which could not be separated in the solid state, and oxidation of the hydrated mixture produced the characteristic odor of camphor, although neither oxime nor semicarbazone could be prepared.

The fourth and largest portion was mainly 1- β -phellandrene, as was also the fifth. The nitrite, which was easily produced from either by the usual methods, melted at 99-100° C. No limonene or dipentene could be detected in any of the terpene fractions, in spite of the characteristic odor.

The portions boiling at 145-208° C. under 45-50 mm. pressure contained most of the ester. After saponification, the aqueous solution was neutralized and precipitated fractionally with silver nitrate. The first 0.5 Gm. contained 43.7 per cent of silver, corresponding to caprylic acid. The chief acid, however, was acetic, identified by odor and conversion to ethyl acetate.

The oil therefore contains approximately 78 per cent of terpenes, over half of which is 1- β -phellandrene and the balance the two pinenes and probably camphene. The other 22 per cent is mostly sesquiterpenes or derivatives, with small amounts of phenols, of esters of acetic and possibly caprylic acids, and of aldehydes and ketones.

SEATTLE, WASH.,
October 1, 1932.

AMPHIACHYRIS DRACUNCULOIDES (DC.) NUTT.*

A STUDY OF THE FLOWERING BRANCHES.

BY LOYD E. HARRIS¹ AND INA GRIFFITH.²

This plant has been called *Brachyris dracunculoides* DC., *Brachyris ramosissima* Hook, and *Amphipappus dracunculoides*, Torr. and Gray (1). Local names used

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² Part of a thesis submitted to the Graduate Faculty of the University of Oklahoma in partial fulfilment of the requirements for the degree of Master of Science in Pharmacy.

in Oklahoma are Broom Weed and August Flowers. It was collected by Nuttall in 1818, on the edge of ponds near Salt River in Arkansas (2). He gave it the present name in 1841 (3). It is widely distributed in Missouri, Kansas, Texas, New Mexico and Oklahoma (4).

Amphiachyris dracunculoides Nutt. has been used many years as a home remedy for coughs and colds. It is administered in the form of a syrup which is prepared by making an infusion from the dried branching portion of the plant including the flowers and leaves. To the tea thus obtained a sufficient quantity of sugar is added to produce a thick syrup. A survey of the literature revealed nothing as to constituents present in this plant.

EXPERIMENTAL.

The flowering top including the small branches and leaves were collected in September while in full bloom, and allowed to dry indoors. This material was then ground to a number 20 powder.

EXTRACTION WITH SELECTIVE SOLVENTS.

Two samples, each weighing 40 Gm. were used and the following results were obtained:

Solvent in Order Used.	Sample No. 1 Wt. in Gm.	Sample No. 2 Wt. in Gm.	Per Cent Sample No. 1.	Per Cent Sample No. 2.
Petroleum ether	2.0	2.0	5.00	5.00
Ether	3.1	3.0	7.75	7.50
Dehydrated alcohol	5.5	5.5	13.75	13.75
Water	5.6	5.9	14.00	14.75
Dil. alkali (0.1 per cent)	4.1	3.9	10.25	9.75
Dil. acid (1.0 per cent HCl)	1.7	2.3	4.25	5.75
Residue	17.8	17.1	44.50	42.75
Total	39.8	39.7	99.50	99.25

The petroleum-ether extract was fatty in nature and became semi-solid on standing. The saponification value of this extract was 158.36 and the iodine value (Hanus) was found to be 38.31.

ASH.

Ash determinations, using three samples were made, with the results tabulated below.

	Wt. of Sample.	Total Ash.	Per Cent.	Water-Soluble Ash. Grams.	Per Cent.
1	1.9192	0.0995	5.18	0.0331	1.72
2	1.9958	0.1063	5.32	0.0402	2.01
3	1.5893	0.0820	5.16	0.0317	1.99
Average	1.8347	0.0966	5.22	0.0350	1.907
		Acid-Soluble Ash. Gm.		Per Cent.	
		0.0368		1.91	
		0.0393		1.96	
		0.0301		1.89	
	Average	0.0354		1.92	

MOISTURE.

Moisture determinations were made using the xylene and oven methods.

	Xylene Method (5).		Oven Method (6) (100° C.).	
	Wt. of sample.	Per cent moisture.	Wt. of sample.	Per cent moisture.
1	9.3678	2.12	9.6933	11.23
2	10.0701	1.98	9.2340	10.90

ALCOHOLIC EXTRACT.

It was believed that the alcoholic extract contained some important constituents. Accordingly thirty-two and three-fourth pounds (14.85 Kg.) of the ground plant material were extracted with U. S. P. alcohol.

The alcohol was recovered by distillation, and the residue extracted with successive portions of petroleum ether to remove any fatty material that had been extracted.

Five hundred Gm. of the residue were washed with distilled water, which process was performed with difficulty since the mass was quite adhesive. The washings were evaporated to a syrupy consistency on a water-bath. During the evaporation a brown material settled to the bottom of the dish. Finally this material was separated from the solution by decanting the clear liquid. The brown material hardened on standing, was soluble in dilute alkali, slightly soluble in hot water, alcohol and chloroform, and insoluble in ether. When tested with Fehling's solution, reduction was observed after a solution of the material had been heated with dilute hydrochloric acid.

The syrupy liquid obtained by decantation was light brown in color and had a very bitter taste. A portion of this was extracted with amyl alcohol. The volume of the alcoholic extract was reduced under diminished pressure. When this concentrated amyl alcohol was set aside and cooled a yellow precipitate formed. The first precipitate obtained in this way, after drying in a desiccator, was a powder. In succeeding attempts it was always pasty. This material was soluble in hot water and hot alcohol but insoluble in ether, chloroform and benzene.

When a solution of this material was tested with Fehling's solution a deposit of red cuprous oxide was obtained. However, when an aqueous solution of this material was treated with lead subacetate, filtered, treated with hydrogen sulphide to remove the lead, the excess hydrogen sulphide removed by boiling, and allowed to react with Fehling's solution, there was no reduction.

This solution was hydrolyzed by the addition of a few drops of hydrochloric acid and boiling for one minute. The solution thus obtained reduced Fehling's solution but no osazone could be obtained. During the hydrolysis a brown material separated which hardened on drying. It melted at 115° C. When mixed with water and titrated with *N*/50 NaOH the results indicated it to have acidic properties.

RESIDUE FROM AMYL ALCOHOL EXTRACT.

The syrupy liquid remaining after extraction with amyl alcohol was next examined. It did not reduce Fehling's solution until after it was hydrolyzed. During the hydrolysis a brown material separated, having the same properties as the similar material mentioned above.

After decolorizing solutions of unhydrolyzed and hydrolyzed materials with "norite" they were examined with a polariscope. The first was inactive whereas

the hydrolyzed solution had a specific rotation of -14.7° . From this same hydrolyzed material an osazone was obtained and after recrystallization a melting point of 212° C. was determined.

There are three known osazones having this melting point, namely, glucosazone, fructosazone, mannosazone. Attempts to obtain saccharic acid from the sugar were unsuccessful. A ketose was indicated by a positive Seliwanoff reaction, however, no osazone could be obtained using methyl phenylhydrazine (7).

The presence of a glucoside has been definitely established but its composition has not yet been determined. Work is to be carried on in this direction during the year 1933.

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- (5) Jenkins and DuMez, "Quant. Pharm. Chem.," page 229.
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THE STORY OF THE ISOLATION OF CRYSTALLINE VITAMIN D₁.

A REVIEW ARTICLE BY K. JOSEPHSON IN *Farm. Revy*, 30 (1931), 566-571.

TRANSLATED BY C. S. LEONARD.

Translator's Note: That Windaus should have been successful in isolating crystalline vitamin D₁ is not surprising. Sterol chemistry has occupied his attention since his early teaching days. His *Habilitationschrift* as Privat Dozent at Freiburg in 1903 was on the subject: Cholesterol. Indeed Freiburg had a tradition in the field, for van Oordt in 1901 under Kiliani's tutelage presented a doctor's thesis from Gatterman's laboratory on cholesterol, as did, in 1905, Windaus' pupil, Gustav Stein. Meanwhile, Windaus began publishing a series of articles in the *Berichte* on the chemistry of this sterol, which led to partial formulation of the structure in 1908. A pupil, Adaml, in 1911 wrote a further dissertation on the subject and again in 1919, 1923 and 1925, Windaus published work on phytosterols. So the important phytosterol, ergosterol, was but one member of a family familiar to this chemist. He began to report on the study in 1923. It was but natural that he should become interested in the subject of isolation of pure crystalline vitamin when the occurrence of the D vitamin had been traced to the sterol portion of the unsaponifiable fraction of fats. This sterol fraction is largely cholesterol and Hess and Weinstock had shown that cholesterol could be activated by light but *not* if pure. The patience and skill which won a Nobel prize is recorded below:

In volume 489 of *Liebig's Annalen* (page 252) Windaus reports that in his work upon ergosterol irradiated with ultraviolet light he has succeeded in obtaining a crystalline vitamin which he calls vitamin D₁. As such a result in the field of vitamin research so intensively followed in recent years ought to interest pharmaceutical workers, a summary of the more essential findings is given.

In January 1927, Windaus (with Hess) determined that ergosterol on irradiation with ultraviolet light forms quite an active antirachitic substance, the D vitamin. From that time an intensive study went on in Windaus' laboratory for the isolation of the vitamin in pure crystalline