THE FATTY OILS OF SWEET CLOVER SEED— I: MELILOTUS ALBUS

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Melilotus albus, commonly called White Sweet Clover, together with more than twenty-five species occurring in the temperate and sub-tropical parts of the world, belongs to the botanical genus Melilotus. Its earliest history is little known. It has been used as a forage crop in Thibet for more than two thousand years. Being a native of Europe and Asia, it has never gained the prominence in its native habitat that it has in most parts of the New World. It probably had its origin in the high plateaus of western Asia, where alfalfa and red clover were first cultivated. It has been known in this country for almost two centuries, being found in Virginia as early as 1739 and in New England in 1785.

Melilotus albus is a biennial clover. Under natural conditions the seedlings appear early in the spring and by fall they may have reached a height of four to five feet. By fall the seedling has produced a large bulky tap root which may often extend to a depth of six to eight feet, as well as an extensive secondary root system. During the second year the plant shows a much larger growth, often reaching a height of eight to ten feet, and produces a number of white, sweet-scented flowers in the form of racemes. During early fall of the second year, they mature an abundance of seed which greatly resembles that of alfalfa. About the time of seed formation, the leaves begin to drop off. The plant contains a bitter substance having an agreeable, aromatic odor. This substance has been identified by other workers as courmarin. The young plant contains but small amounts of courmarin, but as it grows toward maturity, the coumarin content increases. The plant has a rank growth of stems, which rapidly become woody, and after the formation of seed, the plant dies. It belongs to the legume family and carries the same nodular bacteria as does the alfalfa plant.

Very few plants are able to supply as much organic matter to the soil as does the sweet clover. It reaches its optimum development in soils of high lime content. It will grow well on heavy clay soils or in coarse sandy ones. Even extreme alkali content does not inhibit its rapid growth. By reason of its deep root system, it is able to withstand drought as well as alfalfa. It can endure wet soils much better than any of the other clovers. On account of its wide soil range, it becomes a valuable forage crop where alfalfa and other clovers will not grow.

It has a wide climatic adaptation, growing from the Mexican border well into Canada. It endures the cold, dry winters of our northwest without winter-killing and the hot, humid summers of the south do not effect it.

The purpose of this study was twofold: (a) To ascertain whether the

physical and chemical constants of the oil of sweet clover seed grown in this country are similar to those reported by Grimme[1], for seed purchased on the Hamburg market. (b) To determine whether the domestic oil possesses commercial value.

The seed upon which we undertook these studies was produced by the Department of Agronomy of South Dakota State College, at their substation located at Highmore, South Dakota, thus giving it a high-land environment. The seed so furnished us through the courtesy of Dr. A. N. Hume of the above department, was of a yellowish-brown color, resembling that of the alfalfa plant. The seed of the sweet clover plant is quite small; according to Werner one pound of it may contain as many as 235,000 seeds.

Analysis of the Seed. The seed was ground through a common laboratory handmill, to a fine flour. The following table presents the results of analysis of the ground seed, in percentages by weight:

Moisture	6.58
Ether Extract	5.26
Protein	35.17
Crude Fiber	11.15
Ash	3.46
N. F. Extract	48.38

Preparation of the Oil. To prepare the oil for this work we proceeded as follows: The seed was first ground through a common laboratory mill, setting the crushers so as to crack the seed thoroughly, but not to reduce it to a fine flour. This meal was extracted in a specially constructed Soxhlet extraction apparatus. The capacity of the apparatus was approximately two kilograms of the meal. The oil was extracted with ethyl ether. Extraction was considered to be complete when the ether solution left no residue upon evaporation. The ether was now evaporated and the oil filtered through an ordinary filter paper in order to remove any finely ground flour which siphoned over with the oil-ether solution. The oil thus extracted had a greenish-amber color, with the characteristic coumarin-like odor. Its specific viscosity, Sayboldt, at 70° F. was 19.1.

Physical Characteristics of the Oil. The oil was found to be a drying oil, having a specific gravity of 0.9513 at 25° C., as determined by the picnometer. According to the Abbe refractometer, its refractive index was 1.4838 at 25° C.

Chemical Characteristics of the Oil. The saponification number of the oil was 203.3 and the iodine number by the Hanus method, 142.5. The results of these tests indicate a probable composition of the oil similar to that of popyseed oil, as to the nature of the acid groups involved and to its quality as a drying oil. To substantiate further our supposition of its drying quality, we oxygenated the oil by the methods of Livasche[2] and of

Hubl-Lippert.[3] The latter method gave much higher numbers. Thus:

Time of exposure—Days	Gain in % of weight
1	1.42
2	5.30
3	7.66
4	7.99

There was no further gain in weight after the fourth day.

According to the Livasche method we obtained the following results:

Time of exposure—Days	Gain in % of weight
1	3.48
2	3.78
3	3.78
4	3.78
5	4.00
6	4.15

There was no increase in weight after the sixth day.

The above data would rank the oil with the group represented by rapeseed, as to drying properties.

These results were confirmed by applying the elaidin test, using the method of Poutet.[4] At once an orange colored, buttery mass began to form, supernatant upon a watery liquid, and within twenty minutes the reaction was complete. This test would place the oil in the group represented by sesame, rape and sunflower. Its character as a drying oil is thus further established.

The specific Maumene number, as determined by the Woodman method, was 108.4. This still further points to the drying nature of the oil.

The Reichert-Meissl value was determined by the method of Lewkowitsch[5] and was 3.35. This would indicate a saponification number which would probably be above 200, a verification of the saponification number as determined directly.

The saturated and unsaturated (or solid and liquid) fatty acids were separated by the method of Gussarow-Varrentrop, as modified by Tortelli and Ruggeri.[6] By this method we found the oil to contain 78.7% of unsaturated or liquid fatty acids, and 8.2% of saturated or solid acids.

Using the method of Allen and Thomson,[7] we found the unsaponifiable matter to be 3.05 per cent.

The glycerol content of the oil was 11.11 per cent, calculated from its saponification number.

The iodine value (Hanus) and neutralization number were determinded upon the saturated and unsaturated fatty acid fractions as follows:

	Neutralization No.	Iodine No.
Unsaturated acids	198.9	147.16
Saturated acids	216.3	68.05

These results further substantiate the corresponding numbers from the original oil.

From the above neutralization numbers, we calculated the mean molecular weights of the two types of acids, as follows: Unsaturated, 282.1;

saturated, 259.75. It is assumed from these molecular weights that the saturated fraction is largely palmitic acid, and that the unsaturated portion is of the oleic type.

The acetyl value was found to be high; it required 43.13 mg. of potassium hydroxide to neutralize the acetic acid produced from the hydrolysis of one gram of acetylated fat.

The free fatty acids, as determined by the method of Pickering,[8] were 4.08 per cent.

Qualitative Tests. In addition to the above quantitative tests of the oil, certain generic tests of a qualitative nature were made.

The Molisch test for carbohydrates, the ferric chloride test for phenol derivatives, and the phenylhydrazine reaction for ketones, all gave negative results. The Schiff reaction was positive for aldehydes, although these bodies occurred in traces only, insufficient to warrant a quantitative examination.

Summary and Conclusions. The experimental data as presented in this paper warrant the following conclusions: (a) The chemical composition of this oil is markedly different from that reported by Grimme,[9] as shown in the following summarized table:

	S. D. Seed	Grimme
Specific Grav. at 25°C	0.9513	0.9310
Free Fatty Acids	4.08%	7.80%
Saponification Number-Oil	203.3	189.9
Iodine Number	142.5 (Hanus)	71.4 (Wijs)
Unsaponifiable Matter	3.05%	2.05%
Glycerol	11.11%	9.42%
Fatty Acids	86.90%	93.25%
Quality of oil as a dryer	Drying	Non-drying
Sp. Maumene No.	108.4	
Reichert-Meissl No.	3.45	
Neutralization No.—Unsat. Acids	198.9	
Neutralization No.—Sat. Acids	216.3	
Iodine Value (Hanus)—Unsat. Acids	147.16	
Iodine Value (Hanus)—Sat. Acids	68.05	
Mean Molec. Wts.—Unsat. Acids	282.1	
Mean Molec. Wts.—Sat. Acids	259.75	
Acetyl Value	43.13	

Evidently the constants of the oil from this seed, grown under varying conditions as to soil and climate, differ widely.

(b) The above data indicate that this oil possesses commercial value as a substitute for the drying oils.

The oil of Melilotus officinalis will be the subject of a future study.

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[1] Grimme, C. L.: Oils of Papilionaceae, Chem. Rev. Fett. Harz. Ind. 18:53, 77, 1911.
[2] J. Soc. Chem. Ind., 6,494 (1886).
[3] Chem. Revue, 67 (1899).
[4] Annal. d Chim. et Phys. 1838, (69), 44.
[5] Lewkowitsch, Vol. 1, p. 426, 1921 ed.
[6] Lewkowitsch, Vol. 1, p. 560, 1921 ed.
[7] Chem. News, 1881, (43), 267.
[8] Commercial Anal. of Oils, etc., p. 17.
[9] Grimme, C. L.: Oils of Papilionaceae, Chem. Rev. Fett Harz. Ind. 18:53, 77, 1911.