

CHEMICAL EXAMINATION OF THE ESSENTIAL OIL OF *ARTEMESIA SCOPARIA* WALDST AND KIT

BY DHARAM BAL PARIHAR AND SIKHIBHUSHAN DUTT, F.A.Sc.

(Chemistry Department, Delhi University)

Received March 5, 1947

FROM the green herb and the flowering heads of *Artemesia scoparia* Waldst and Kit, Parihar and Dutt¹ have already reported the isolation of two interesting compounds, one a crystalline lactone, which they named 'Scoparine' (M.P. 146° C.) with the molecular formula $C_{16}H_{20}O_5$ and the other a pleasant smelling essential oil. In view of the small quantity and yield of the essential oil obtained, it was not possible to work out its constituents at the time of the last communication.

In the present work however larger quantities of the raw material were available and 8.53 kilos of the air-dried plant after the removal of Scoparine in the manner already described in the previous communication, 64 c.c. of a deep green essential oil with a refreshing fragrance were obtained by a steam distillation of the residue, thus giving an yield of 0.75 per cent. The residual mass after drying and extracting with ether in the cold gave 380 gm. of an highly viscous deep green fatty matter (M.P. 49–51° C.) in an yield of 4.45 per cent. The systematic examination of the fat has been reserved for a separate communication, while in the present one the essential oil has been worked out in detail.

The present authors while working on the essential oil of the plant isolated from it two important constituents, one from the phenolic portion identified as eugenol and the other from the non-phenolic portion identified to be a sesquiterpene having a molecular formula $C_{15}H_{24}$. The latter compound although having physical properties very similar to caryophyllene, does not appear to be identical with this substance or for that matter any other known sesquiterpene, as its nitrosate and nitrosite, isolated by the present authors have got quite different properties. This sesquiterpene has therefore been named "Scoparilene".

EXPERIMENTAL

Isolation of the essential oil of Artemesia scoparia.—8.53 kilos of the powdered and air-dried plant were extracted with hot alcohol under reflux in lots of 1 kilo at a time. The extracts were filtered hot and the solvent

distilled off on a water-bath. The syrupy concentrate was allowed to stand overnight, when Scoparine separated out. It was filtered off through Buchner's funnel and washed with a little petroleum-ether. The mother-liquor and the washings were mixed and freed from petroleum-ether by distillation. The residual mass was subjected to steam distillation in a five litre pyrex flask. The essential oil separated from the aqueous distillate as a green pleasant smelling oil. The separated oil was decanted off, dried over anhydrous magnesium sulphate and filtered through filter-paper. Thus 64 c.c. of the essential oil was obtained in an yield of 0.75 per cent. on the weight of the dried stuff. The residual mass after drying was extracted with ether in the cold and the solvent distilled off. In this way, a deep green highly viscous fixed oil (M.P. 49.51° C.) was obtained in an yield of 4.45 per cent.

The essential oil was found to have the following physical and chemical constants:—

Refractive Index (23° C.)	=	1.5220
Specific gravity (23° C.)	=	0.9497
Saponification value	=	77.28
Acid value	=	6.3
Rotation		nil
Saponification value after acetylation			..	=	38.4

The oil gave a deep green colour with alcoholic ferric chloride indicating the presence of a phenolic compound in the oil.

Separation of the phenolic portion.—58 c.c. of the oil were treated with 5% sodium hydroxide solution in a separating funnel, and after shaking the oily layer which got separated on standing was removed. The alkaline solution was acidified with dilute hydrochloric acid and the oily layer which separated was extracted with ether washed with water dried and the solvent distilled off. It was further dried over anhydrous magnesium sulphate, thereby giving an ultimate yield of 5.2 c.c. of the phenolic compound. The compound had a strong clove-like smell. With alcoholic ferric chloride it gave a green colour. Under ordinary pressure it was found to boil at 250°–52° C. with decomposition. B.P. 144–46° at 5 mm.

Preparation of the benzoyl derivative.—1 c.c. of the substance was dissolved in 20 c.c. of a 3 per cent. caustic soda solution in a test-tube and 1 c.c. of benzoyl chloride added to the same. After vigorous shaking the mixture was allowed to stand overnight, when a crystalline compound settled down. It was filtered, washed first with one per cent. solution of

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caustic soda, then with water and finally dried. It was recrystallised from dilute alcohol in shining white needles melting sharp at 69° C.

The substance was thus identified to be eugenol.

Examination of the non-phenolic portion.—The non-phenolic portion was washed with water and dried over anhydrous MgSO₄. 62 c.c. of this portion were then subjected to fractional distillation at 5 mm. pressure. The various fractions obtained are given below:—

TABLE II

Fraction No.	Boiling range	Volume of distillate
1	118–47° C. ..	1.5 c.c.
2	147–48° C. ..	45.4 ,,
3	Residue (Solid) ..	3.3 ,,
4	Experimental loss ..	1.8 ,,

Fraction No. 1.—This was a colourless oil and had a peculiar pleasant odour. It had a refractive index (18° C.) 1.5020, and saponification value 17.2. It adds on bromine in acetic acid and develops light pink colour with Schiff's reagent after five minutes. It did not form any acetyl compound nor did it give any semicarbazone, or oxime. It was identified to be a hydrocarbon. The quantity was, however, too small for systematic examination.

Fraction No. 2.—It was a colourless fragrant oil with the following physical and chemical constants:—

Specific gravity (15° C.)	= 0.9166
Refractive Index (18° C.)	= 1.5225
Optical rotation	= nil
Acid value	= nil
Saponification value after acetylation ..	= 22.1
Saponification value	= 11.2

The compound is unsaturated and adds on bromine in acetic acid. It gives deep pink colouration with conc. sulphuric acid which is characteristic of sesquiterpenes. It gives a light pink colour after two minutes with Schiff's reagent, and has no action on Tollen's reagent. Under ordinary pressure it boils at 252–54° C. Repeated attempts to acetylate and benzoylate the compound were unsuccessful. The compound did not give any oxime or semicarbazone (Found: C= 88.21, 88.14; H= 11.68, 11.74;

$C_{15}H_{24}$ requires C = 88.23, and H = 11.76 per cent.) It is evidently a sesquiterpene hydrocarbon and has been named "Scoparilene".

Scoparilene nitrosite.—5 c.c. of glacial acetic acid were cautiously added to a mixture of 5 c.c. Scoparilene, 12 c.c. petroleum-ether and 5 c.c. of a saturated solution of sodium nitrite in a test-tube. On gentle scratching of the sides of the tube a gradual separation of a crystalline nitrosite took place. It was filtered off, washed with a little water and crystallised from alcohol. It crystallises in shining pale green needles melting sharp at $111^{\circ}C$. The substance was found to be different from the nitrosite of caryophyllene.

Scoparilene nitrosate.—A solution of 5 c.c. of conc. nitric acid in 5 c.c. of glacial acetic acid was carefully added to a well-cooled mixture of 5 c.c. Scoparilene, 5 c.c. glacial acetic acid and 5 c.c. amyl nitrite in a test-tube. Finally 5 c.c. of alcohol were added and the sides of the test-tube were scratched. After two hours, the nitrosate, which separated out, was filtered off, and washed with a little water. The compound was recrystallised from hot alcohol in shining needles melting sharp at $216^{\circ}C$. This was found to be different from the nitrosate of caryophyllene.

Fraction No. 3.—It was a deep pink coloured solid mass mainly composed of the decomposed products.

SUMMARY AND CONCLUSION

1. From the green herb and the flowering heads of *Artemisia scoparia* an essential oil and a fixed oil have been obtained in yields of 0.75 per cent. and 4.45 per cent. respectively.

2. The essential oil was found to contain eugenol (8.96%), a sesquiterpene (79.44%), a hydrocarbon (2.63%), and residue mainly containing the decomposed products (8.97%).

3. The sesquiterpene, which has a molecular formula $C_{15}H_{24}$ has been named "Scoparilene". It has been found to be different from any known sesquiterpene. Its nitrosate and nitrosite have been prepared and described.

REFERENCES

1. *Proceedings of the Indian Academy of Sciences*, 1947, XXV, 153.