## STUDIES ON THE ESSENTIAL OILS OF THE PAKISTANI SPECIES OF THE FAMILY UMBELLIFERAE

## Part XIV. Dorema ammoniacum ("Ushak") gum

## MUHAMMAD ASHRAF, ARSHAD MUNIR, AMNA KARIM and MUHAMMAD KHURSHID BHATTY

## PCSIR Laboratories, Lahore-16 (Received February 19, 1977; revised April 4, 1977)

Abstract. The essential oil distilled from the gum of *Dorema ammoniacum*, with an yield 0.48% has been characterised physico-chemically and studied with respect to its chemical composition for the first time. The oil has been found to contain hydrocarbon fraction (28.0%) with ferulene being the major component (19.6%), while the oxygenated fraction is composed of linally acetate (1.2%), citronelly acetate (38.6%), doremone and doremyl alcohol (4.2%), doremyl alcohol (12.7%) and coumarins (15.0%). The oil is similar to its kind produced elsewhere in the world.

Dorema ammoniacum is native to Pakistan, Afghanistan and Iran. In Pakistan, it grows wild in the Baluchistan Province. The plant exudes a yellowish white gum, ammoniacum, at the flowering stage whose therapeutic value has since long been recognized and is referred to in different systems of medicine.<sup>1</sup> The gum also finds application in confectionery, baked food and occasionally in soap and perfumery.

The essential oil of the gum, which is available in large quantities in Pakistan has yet not been investigated with regard to its quality and chemical composition. These studies were, therefore, carried out with a view to evaluating the commercial importance of the gum which may find ready acceptability in the international markets. This paper sums up the results of our studies on the essential oil of the gum.

### **Materials and Methods**

The essential oil from the gum was recovered by dry steam distillation according to the method already discussed in Parts I and II of this series.<sup>2,3</sup>

#### Results

# TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL PROPERTIES OF THE ESSENTIAL OIL OF DOREMA AMMONIACUM GUM.

Distillation time	60 hr
Yield	0.48%
Colour	Pale yellow
Specific gravity	0.864832
Refractive index	1.471032
Optical rotation	0°
Acid value	1.27
Ester value	70.50
Ester value after acetylation	100.60

The gum was distilled for 45 hr and the essential oil recovered by extraction of the distillate with diethyl ether. On removal of the solvent the oil was recovered in 0.48% yield. The physico-chemical characteristics of the oil as determined according to the methods described earlier<sup>2,4</sup> are shown in Table 1.

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As usual, the oil was separated into hydrocarbon fraction and oxygenated components by column chromatography using silica gel as an adsorbent. Various fractions collected from the column were examined by TLC and ir and the like fractions combined for the identification of individual components.

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF DOREMA AMMONIACUM GUM AS DETERMINEDBY COLUMN CHROMATOGRAPHY.

Solvent used	Component P	ercentage
n-Hexane	Total hydrocarbons	28.0
	α-Pinene	4.1
	β-Pinene	0.8
	Unknown monoterpen	e 1.6
	Unknown sesquiterpen	es 0.9
	Ferulene	19.6
2% diethyl ether in <i>n</i> -hexane	Linalyl acetate	1.2
2% diethyl ether in <i>n</i> -hexane	Citronellyl acetate	38.6
5-10% diethyl ether in <i>n</i> -hexane	Doremone and doremy alcohol	1 4.2
10-50% diethyl ether in <i>n</i> -hexane	Doremyl alcohol	12.7
100% diethyl ether	Mixture of coumarins	15.0
,0	Unrecovered material	0.3

The hydrocarbon fraction was analyzed by GLC using nitrogen carrier gas, flame ionization detector and a stainless steel column  $(3 \text{ mm} \times 3 \text{ m})$  packed with 7.5% carbowax on celite. The individual components were identified against their standard samples.

The oxygenated components were identified by TLC, ir and by preparing their known derivatives.

The chemical composition of the essential oil thus determined is recorded in Table 2.

#### Discussion

The physico-chemical characteristics of the essential oil of the *Dorema ammoniacum* gum are comparable with those given for similar oils in literature.<sup>5</sup> Quantitatively, the constituents of the Pakistani oil are mostly the same as those of similar oils produced elsewhere and reported in literature.<sup>5</sup>

The hydrocarbon fraction of the oil, amounting to 28.0% was resolved into monoterpenes and sesquiterpenes by GLC and the results thus obtained are listed in Table 2. The fraction was also separated into low- and high-boiling constituents by fractional distillation under reduced pressure. The monoterpene fraction (b.p. 72°) and the high boiling fraction (b.p. 99-100°), constituting about 70% of the total hydrocarbon fraction, contained a mono-cyclic disesquiterpene, ferulene; ir (3.5, 6.9, 7.3, 11.4, 12.6, 14.5 µm). It was tentatively identified by its refractive index, 1.48626<sup>20</sup> (lit.<sup>5</sup> 1.48423<sup>20</sup>).

The oxygenated fractions of the oil consisted of linalyl acetate, citronellyl acetate, doremone, doremyl alcohol and a mixture of coumarins. The first fraction contained a mixture of two esters, *viz.*, linalyl acetate and citronellyl acetate. The esters were separated from each other by rechromatography and identified by ir comparison with the standard spectra. Roesnisch<sup>6</sup> has also reported the presence of linalyl acetate and citronellyl acetate in the essential oil of the *Dorema ammonjacum*.

The second fraction (38.0%) of the total oil) gave citronellyl acetate which was hydrolyzed with 0.5N KOH and the alcohol thus obtained was identified as citronellol by TLC and ir comparison.

The next fraction gave a mixture of two compounds. It was rechromatographed to separate the hydroxy and ketonic components. The hydroxy compound was oxidized by John's Reagent to carbonyl compound whose semicarbazone derivative melted at 122-23°, which m.p. is identical with that of the semicarbazone derivative of doremone (lit.<sup>5</sup> 124°). Therefore, the alcohol was identified as doremyl alcohol : ir  $(3.0, 3.5, 6.9, 7.4, 8.6, 10.4, 14.0 \,\mu\text{m})$  by TLC comparison with its sample obtained by converting doremyl alcohol into doremone as described earlier.<sup>5</sup>

The last fraction was a mixture of coumarins; bergaptene and imperatorin were the only identifiable furocoumarins, which were separated by preparative TLC and identified by comparison with their standard samples. The ir spectrum of the last fraction gave a close resemblance with the standard spectrum of ferulic acid but its presence could not be confirmed.

The results of the present studies are in good agreement with the earlier workers.<sup>5,6</sup> However, Roesnisch<sup>6</sup> has reported a very small amount of doremyl alcohol in the essential oil of the *Dorema* ammoniacum gum while doremone was the major constituent (22.0%) of the oil. In contrast, our oil contains 12.5% doremyl alcohol and a very small amount of doremone (3.0%). This difference in the results may be explained on the basis of natural phenomenon by which certain components of an essential oil in the plant are oxidized or reduced. It is possible that the climatic conditions may be favourable for the reduction in our case thus reducing doremone to doremyl alcohol. The oil, nevertheless, can find application in perfumery and medicine.

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