

# THE IDENTIFICATION OF *d*- $\alpha$ -PHELLANDRENE IN THE ESSENTIAL OIL OF LEAVES OF BEL, *ÆGLE MARMELLOS*

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## SUMMARY

The presence of *d*- $\alpha$ -phellandrene in the essential oil of Bel, *Aegle marmelos*, has been definitely established by preparing the maleic anhydride adduct of the terpene and observing the muta-rotatory property of its nitrosite. The leaves of Bel are thus shown to be a rich and convenient source of this unstable terpene.

*Aegle marmelos*, popularly known in Hindustani as Bel and in Sanskrit as Bilwa, is a tree which is indigenous to India and belongs to the Rutaceæ family.<sup>1</sup>

By distillation of the leaves of this tree, Ritsemma<sup>2</sup> obtained an essential oil, in 0.6 per cent. yield, in which he identified limonene. Recently, Baslas and Deshapande<sup>3</sup> have also isolated the essential oil from the Indian tree in 0.6 per cent. yield. The physical properties of these two oils are given below for comparison.

No.	Constant	Indian Bel oil isolated by Baslas and Deshapande <sup>3</sup>	Bel oil obtained by Ritsemma <sup>2</sup>
1	Density .. ..	D <sup>26°</sup> , 0.8476	D <sup>25°</sup> , 0.856
2	Refractive Index .. ..	<i>n</i> <sup>31°</sup> , 1.4750	..
3	Optical Rotation .. ..	+52.1	[ $\alpha$ ] <sub>D</sub> <sup>20</sup> , 10.71
4	Acid Value .. ..	2.9	..
5	Saponification Value .. ..	16.1	..

The latter authors have exhaustively studied<sup>3,4</sup> the Indian Bel oil and reported the presence of *d*- $\alpha$ -phellandrene, *p*-cymene, cineol, citronellol, citral and cuminaldehyde. The interest of the present author was confined

only to *d*- $\alpha$ -phellandrene which had been reported to be the chief constituent, consisting at least of 35 per cent. of this oil. Phellandrene being one of the unstable terpenes, the leaves of Bel which can be collected in abundance might be regarded as a rich and convenient source for it. However, the existence of this terpene in the Bel oil has not been conclusively proved, and it was with a view to adducing further evidence in this respect that the present piece of investigation was undertaken.

Baslas and Deshapande<sup>3,4</sup> have inferred the existence of this terpene mainly on the basis of (i) the physical properties of their so-called 'phellandrene-fraction,' and (ii) the m.p. of the nitrosite obtained from it; both of which are not sufficient; because their phellandrene-fraction, according to their own later<sup>4</sup> observations, was in fact a mixture, containing *p*-cymene; and as Guenther<sup>5</sup> has rightly remarked, the nitrosites, ordinarily used in the past to characterise  $\alpha$ -phellandrene, have dubious value as criteria of purity. Thus it has been shown by several investigations that the  $\alpha$ - and  $\beta$ -nitrosites are formed together<sup>6-9</sup> and a tedious procedure<sup>10</sup> has to be followed before the two compounds can be separated, and even then there is no guarantee, regarding their purity. The difficulty is further enhanced by the fact that the  $\beta$ -isomer is labile and undergoes 'transmutation' under the conditions used for its purification.<sup>10</sup>

In the work which follows, special emphasis has been laid on those properties of phellandrene which when applied to the present case, will not leave any doubt with regard to the existence or non-existence of this terpene in this oil. One such property is due to the conjugated system of double bonds by virtue of which the terpene can add on to  $\alpha$ - $\beta$ -unsaturated carbonyl compounds. Thus Diels and Alder<sup>11</sup> prepared an adduct, m.p. 126-7°, by treating the terpene phellandrene with maleic anhydride. Birch<sup>12</sup> utilised this reaction to develop a neat method for the determination of *d*- and *l*-isomers as well as to establish the presence of the racemic forms by means of the mixed melting points of the adduct. Kaufman, Baltes and Joseph,<sup>13</sup> and Goodway and West<sup>14</sup> describe the determination of the diene number for the phellandrenes which may be a very useful index of purity. It has been found that the 'diene number and optical rotations are linear variants.'<sup>15</sup> Goodway and West<sup>16</sup> also determined the proper conditions under which only the  $\alpha$ -phellandrene would react with maleic anhydride, while the  $\beta$ -isomer remained unaffected. They were thus able to prepare separative derivatives for this terpene.

The essential oil, used in the present investigation, was obtained by hydro-distillation of the leaves of the same Bel tree as the one whose leaves

were used by Baslas and Deshapande (*loc. cit.*). The oil was obtained as a light-yellowish layer floating over the aqueous distillate from which it was removed and dried over anhydrous sodium-sulphate. It was then distilled under reduced pressure to remove the mono-terpene portion which was then distilled twice at atmospheric pressure when the fraction, b.p. 173–75°/750 mm. was obtained. This was supposed to contain *d-a*-phellandrene. It gave an orange coloration with diazotised *p*-nitro-aniline, indicating the presence of a conjugated double bond.<sup>17</sup> Next the fraction was treated with equimolecular proportion of maleic anhydride in dry benzene solution, when an adduct, m.p. 126°, was obtained. Melting point of *a*-phellandrene adduct is also 126°. This confirmed the presence of *a*-phellandrene in the essential oil of Bel leaves.

An additional support was sought through the study of the optical rotation of the nitrosite, m.p. 120°, obtained from the same fraction, 173–75°/750 mm., after four purifications with chloroform and methyl alcohol. Thus it was observed that the specific rotation of the nitrosite was opposite in the sense to that of the terpene. Further, it showed muta-rotation, the rotation changing from  $-47^\circ$  to  $+42.6^\circ$  in three days. This is one of the rare properties exhibited by a terpene compound, and is in agreement with the observations made by Read and Storey.<sup>16</sup> Baslas<sup>20</sup> has confirmed the fact that the nitrosite of the above fraction shows muta-rotation.

#### EXPERIMENTAL

*Preparation of the maleic anhydride adduct.*—The fraction (5 g.) and maleic anhydride (3.8 g.) were mixed with dry benzene (25 c.c.) in a thick-walled 100 c.c. stout pressure bottle which was afterwards properly corked and then heated for five hours in a boiling water-bath. The bottle was then gradually cooled and brought to the room temperature during four hours, then opened and the contents filtered to separate suspended solids. The solution was then chilled in water to about 10°. The solid (3.8 g.) which separated was filtered out. The crude solid compound melted at about 120°, but after two crystallisations it was obtained as white needles, m.p. 126° (Found: C, 71.52; H, 7.8;  $C_{14}H_{18}O_3$  requires C, 71.79 and H, 7.7 per cent.).

*Optical rotation of the nitrosite.*—The nitrosite has  $[\alpha]_D$ ,  $-47^\circ$  (in chloroform,  $c$ , 2.936;  $l$ , 2 d.m.; and  $a$ ,  $-2.76^\circ$ ) which changed to  $+42.6^\circ$  in three days ( $c$ , same,  $l$ , same, and  $a$ ,  $+2.5^\circ$ ).

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