# CONSTITUENTS OF THE ESSENTIAL OILS FROM TWO VARIETIES OF *CYMBOPOGON DISTANS*

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*Cymbopogon distans* (Steud.) Wats. (1), unlike other species of the series Citrati, has linear-to-filiform leaf blades and a shallowly concave lower glume of the sessile spikelet (1). Both of the varieties of *C. distans* reported in the present investigation grow wild in the Himalayan region. In our earlier communication, we had reported the chemical composition of *C. distans* (2), a species growing around Nainital. We have now identified its major constituent, $C_{15}H_{24}O$, as α-oxobisabolene. The second chemotype of *C. distans* was collected from Munsiyari, and the results presented herein account for ca. 80% of the oil obtained from this chemotype. Its major constituents were observed to be citral, geranyl acetate, and geraniol; however, α-oxobisabolene was not detected in this variety.

## RESULTS AND DISCUSSION

The physico-chemical properties and chemical composition of the oils isolated from two morphologically identical varieties of *C. distans* varied markedly.

*C. DISTANS* (Nainital collection).—The oil (0.6% by weight of fresh aerial part) had a specific gravity of 0.801, an acid value of 1.15, an ester value of 19.6 (ester value after acetylation 80.95), and a carbonyl value of 5.1 (as $C_{10}H_{16}O$). The gc and gc/ms analysis of the oil showed the presence of 12 monoterpene (28.4%) and 13 sesquiterpene (32.8%) hydrocarbons; the remaining 38.8% was assigned to oxygenated compounds (2). The major sesquiterpenoid, suspected earlier to be an alcohol, contained alcohol as an impurity. This major component has now been isolated and identified as α-oxobisabolene on the basis of its uv, ir, $^1$H-nmr, and ms data. Further, the plants collected during different months, from March to November, showed significant variation in the yield of oil (0.2% in March to 0.6% in November) as well as α-oxobisabolene (18% in March to 68% in November), which was always the major component in the oil. The gc of the oil samples also showed the absence of citral, geraniol, and geranyl acetate.

Ours is the first report of the isolation of α-oxobisabolene from any variety of *Cymbopogon* known to grow in India. The other two species reported to contain α-oxobisabolene are *Stevia purpurea* (3) and *Cymbopogon citratus* growing in Ethiopia (4).

*C. DISTANS* (Munsiyari collection).—The essential oil (0.6% by weight of aerial part) from this species had a specific gravity of 0.927, an acid value of 4.34, a carbonyl value of 33.16, and an ester value of 48.98 (ester value after acetylation 116.17). The oil possessed the characteristic flavor of lemon grass. The major constituents were separated and identified as citral (35%), geranyl acetate (15%), and geraniol (9.5%). Seventeen compounds (80% of the oil), identified by gc/ms and other spectral methods, are given in Table 1. This oil chemically resembles the lemon-grass oil composition.

It is interesting to note that the specimens of *C. distans* collected from two different places show altogether different patterns with respect to their oil composition and, therefore, are chemically different races. α-Oxobisabolene and citral may be used as markers for the chemotypes collected from Nainital and Munsiyari, respectively. The citral-containing wild species can also be of commercial interest due to its wild growth in mountainous wastelands of the Himalayas.

The species Citrati includes lemon grass and citronella grass, which contain citral, geraniol, and geranyl acetate as their principal essential oil constituents, while the species belonging to series Cymbopogon, such as *Cymbopogon stracheyi* and *Cymbopogon jwarancusa*, possess piperitone as the major constituent of their essential oils. Gupta had included *C. distans* in the series Cymbopogon (5); however, based on morphological affinity studies, Soenarko (1) has included this species in the series Citrati. Additionally, our observation of the absence of piperitone in the *C. distans* oils presented in this communication seems to further justify their inclusion in series Citrati.

## EXPERIMENTAL

PLANT MATERIAL.—*C. distans* was collected from Hanumangarh (Nainital, 1900 m) and Munsiyari (Pithoragarh, 2200 m) in different months. The identification of the plants was confirmed by Drs. P.S. Green, T.A. Cope, and S. Dransfield, Royal Botanical Gardens, Kew (voucher nos. H/257/79 and H/1542/83).

TABLE 1. Composition of the Essential Oil of *Cymbopogon distans* (Munsiyari)

| Compound | oil (%) | Method of Identification |
|---|---|---|
| Hydrocarbons | | |
| Camphene | 0.9 | ms |
| Myrcene | 3.4 | ms |
| Limonene | 5.0 | ms |
| α-Pinene | 0.9 | ms |
| β-Pinene | 2.3 | ms |
| *trans*-Farnesene | 2.3 | ms |
| Unidentified Compounds | 10.5 | — |
| Oxygenated Compounds | | |
| Linalool | 2.3 | ms |
| Borneol | 0.7 | ms |
| Isoborneol | 1.1 | ms |
| Citral (a & b) | 35.0 | ms, $^1$H nmr, ir, uv |
| Geraniol | 9.5 | ms, $^1$H nmr, ir, uv |
| Geranyl acetate | 15.0 | ms, $^1$H nmr, ir, uv |
| β-Bisabolol | 0.5 | ms |
| Farnesal | 0.5 | ms |
| Nerolidol | 0.3 | ms |
| Farnesol | 0.3 | ms |
| Unidentified Compounds | 9.5 | — |

ESSENTIAL OIL ISOLATION.—The essential oils were extracted with pentane from the steam distillate of the aerial parts of fresh plants. The extracts were dried over anhydrous $Na_2SO_4$ and the solvent distilled. The physico-chemical properties were determined by classical methods (6).

GAS CHROMATOGRAPHIC ANALYSIS.—Gc analysis was performed on a Varian 3700 gas chromatograph controlled by a Varian CDS-111 microprocessor, using a 35-m glass capillary column coated with OV-101 and an FI detector. The column temperature was maintained at 60° for 5 min and then programmed at 2°/min for the next 75 min and then maintained at 210° for 10 min.

GC/MS ANALYSIS.—The oils were analyzed by gc/ms (70 eV under ei conditions) using J & W fused silica capillary column (liquid phase DB5, column dimension 30×0.25 mm) with He as carrier gas (10 psi). The column temperature was maintained at 60° for 1 min and then programmed at 2.5°/min for the next 29 min and 3°/min up to 60 min. The constituents of the oil were identified by comparison of the mass spectra with those published in the literature (7-12).

Perkin-Elmer 298 IR spectrophotometer was used to record ir spectra. Hitachi 220 UV-Vis spectrophotometer was used to record uv spectra. $^1$H nmr were recorded on a Varian EM 360L (60 MHz) spectrometer in $CDCl_3$ and TMS as internal standard.

ISOLATION OF α-OXOBISABOLENE.—The oil (3 ml) from *C. distans* (Nainital collection) was chromatographed on silica gel (120 g). Elution was carried out by n-hexane (500 ml) followed by increasing concentration of EtOAc in n-hexane (500 ml, 5-50%). The n-hexane-EtOAc fractions containing ketone were concentrated. The compound was finally purified by hplc, using $CHCl_3$ on a μ-Porasil column.

This compound, $C_{15}H_{24}O$, was identified as α-oxobisabolene on the basis of spectral data (uv, ir, $^1$H nmr, and ms), which were identical with those reported in the literature (3,4). The compound formed a 2,4-dinitrophenylhydrazone, mp 188° (uncorr.).

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# ALKALOIDS OF *TYLOPHORA MOLLISSIMA*[1]


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The genus *Tylophora* comprises some 50 species, and most of the known phenanthroindolizidine alkaloids have been obtained from *Tylophora asthmaticus* Wight et Arn. and *Tylophora crebriflora* S.T. Blake (1,2). We report here the chemical examination of the alkaloidal fraction from *Tylophora mollissima* Wt., a slender climber found twining among bushes. The plant was found to have a low alkaloid content (0.01%). Chromatographic separation of the crude basic fraction yielded caffeine as the major constituent and tylophorine and tylophorinine as very minor constituents. All three compounds were identified by direct comparison (mmp, uv, ir, and ms) with authenic samples. These three compounds represent the total alkaloidal fraction.

Although caffeine has been isolated from plants belonging to a variety of families (3), this is the first report of its isolation from a plant of the Asclepiadaceae family.

## EXPERIMENTAL

PLANT MATERIAL.—The plant, collected from the Western Ghats at the Pulney and Sirumalai hills of Madras State, was identified by the late Professor B.G.L. Swamy, and an herbarium specimen is available at Presidency College, Madras.

EXTRACTION AND ISOLATION.—The powdered, whole plant (5 kg) was defatted with petroleum ether and then extracted with EtOH in the cold thrice by percolation. The EtOH extracts were combined, concentrated in vacuo to a syrup, decanted from tarry material, and then treated with 0.5 N HCl. The acid solution was filtered and extracted with $Et_2O$ to remove the chlorophyll. The aqueous solution solution was cooled, basified with $NH_4OH$, and extracted with $CHCl_3$. Evaporation of the $CHCl_3$ extract gave a gum (0.5 g). This was chromatographed over silica gel in $CH_2Cl_2$, and the column was eluted with increasing amounts of MeOH. The early fractions gave caffeine (150 mg), mp 238° [lit. (4), 238°], while the later fractions gave tylophorine (15 mg), mp 286-287° (dec.) [lit. (5,6), 286-287° (dec.)] and tylophorinine (10 mg), mp 246-247° (dec.) [lit. (5,7), 248-249° (dec.)].

Details of the extraction and isolation are available from the senior author.


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