

# ISOLATION OF THE POSTULATED PRECURSOR OF *NOR*-PATCHOULENOL IN PATCHOULI LEAVES

E. TRIFILIEFF

Laboratoire de Chimie Organique des Substances Naturelles, Associé au CNRS, Institut de Chimie, Université Louis Pasteur, 67008 Strasbourg, France

(Received 28 February 1980)

**Key Word Index**—*Pogostemon cablin*; Labiatae; sesquiterpene; biogenesis; patchoulan-1,12-diol.

**Abstract**—Patchoulan-1,12-diol, postulated to be the biogenetic precursor of *nor*-patchoulenol, has been isolated in the leaves of patchouli.

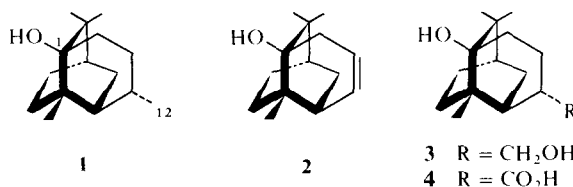
Patchouli oil is important in perfumery. Its major constituent, patchoulol **1**, is practically odourless when pure, and the principal odour carrier of the oil is *nor*-patchoulenol **2** [1, 2]. This  $C_{14}$  tricyclic alcohol, a very minor constituent, has been obtained by total synthesis [3–5]. It may well be a normal metabolite, in the plant *Pogostemon cablin* Benth. (= *P. patchouli* Pellet), of patchoulol. This postulate had led us previously to investigate the metabolism of patchoulol in living organisms. Mammals hydroxylate patchoulol to the corresponding diol **3**, itself being further oxidized *in vivo* to the corresponding acid **4**; we had chemically converted **4** into *nor*-patchoulenol **2** [6]. This is, of course, not necessarily pertinent to the biosynthesis of *nor*-patchoulenol in the plant. We now report the isolation of the diol **3** in the leaves of patchouli.

The methanol extract of patchouli leaves gave, after repeated chromatography, the diol **3**, identified by the identity of its  $^1H$ NMR spectrum with an authentic specimen. The ether extract of the same leaves also contained small amounts of the diol **3**, identified by gas chromatography (co-elution on two columns) and mass spectrometry of its 12-acetate. This isolation lends support to the biogenetic hypothesis mentioned above but does not help to facilitate the supply of *nor*-patchoulenol: the total content of the leaves in the diol **3** is lower than ca 0.02%.

## EXPERIMENTAL

The commercial dry and crushed leaves of patchouli (360 g) were extracted in a Soxhlet, in succession, with hexane, Et. O and MeOH. Column chromatography of the ether extract (4.3 g) on Si gel was monitored by TLC and gave one fraction of the same  $R_f$  as the authentic diol **3** [6]. This was acetylated ( $Ac_2O$ /pyridine, room temp.) and the presence of the monoacetate of **3** was proved by co-elution in GLC [10% SE-30 packed column, and poly-(phenylmethylsiloxane) WCOT capillary column] and by the identity of retention time and fragmentation pattern in GC-MS.

The methanol extract was treated with cold EtOAc: part of it remained insoluble. The EtOAc-soluble part (1.14 g) was chro-



matographed on a column of Si gel with TLC monitoring. The fraction of same  $R_f$  as the diol **3** was chromatographed on PLC, and then injected in an analytical HPLC (Waters Associates, 6000A pump, U6k injector; Siemens differential refractometer, analytical Si gel column  $30 \times 3.9$ ; eluent 40% EtOAc in hexane, 2 ml/min). Eight peaks were detected, the major one having the same elution time as the authentic diol **3**. Successive elutions gave the corresponding substance (3 mg), the 90 MHz  $^1H$ NMR ( $CDCl_3$ ) spectrum of which was identical with that of **3** [ $\delta$  0.88 (s, 3H), 1.09 (s, 6H), 3.47 ( $J = 7.3$  Hz, 2H)].

**Acknowledgements**—I am grateful to Professor Guy Ourisson for helpful discussions and thank Dr. P. Teisseire (Roure-Bertrand, Grasse) for supplying the patchouli leaves. The first indications of the probable presence of patchoulan-1,12-diol in patchouli leaves had been obtained in 1978 by Dr. Luu Bang and Mrs. C. Rakotobe-Ramiliarison in our laboratory.

## REFERENCES

1. Teisseire, P., Maupetit, P. and Corbier, B. (1974) *Recherches* **19**, 8.
2. Teisseire, P., Maupetit, P., Corbier, B. and Rouillier, P. (1974) *Recherches* **19**, 36.
3. Teisseire, P., Pesnelle, P., Corbier, B., Plattier, M. and Maupetit, P. (1974) *Recherches* **19**, 69.
4. Oppolzer, W. and Snowdon, R. (1978) *Tetrahedron Letters* 3505.
5. Pélerin, G. (1980) Dr. Sc. Dissertation, Université d'Aix-Marseille-III; Bertrand, M., Teisseire, P. and Pélerin, G. (1980) *Tetrahedron Letters* 2051.
6. Luu, B., Ourisson, G. and Teisseire, P. (1975) *Tetrahedron Letters* 2211.