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P-MENTHANE-8-THIOL-3-ONE,
A NEW COMPONENT OF BUCHU LEAF OIL

D. Lamparsky and P. Schudel
Givaudan-Esrolko Ltd. Research Company
CH 8600 Dübendorf-Zürich, Switzerland.

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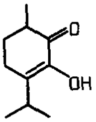
Buchu Leaf Oil is obtained by steam distillation of the leaves of Barosma betulina Bartl., Barosma crenulata (L.) Hook or Barosma serratifolia Willd., originating in South Africa. Depending on the species, the yield of the oil amounts to 0,8 - 2,5% [1] . It is used by the flavour and fragrance industry, because of its characteristic, powerful and fresh odour note. We have therefore been interested in identifying the specific ingredients of the oil which are responsible for its peculiar odour.

Buchu Leaf Oil has already been investigated repeatedly by various authors who have isolated its principal components and determined their structures [2,3,4] . However, none of the hitherto known substances exhibits in isolated form or in combination with other constituents of the oil the typical odour properties we were looking for.

By means of distillation and chromatography, Buchu Leaf Oil [5] was therefore separated into numerous fractions. Comparative odour description lead us among others to the supposition that the compounds searched for within the chromatographic fractions exhibiting the most typical odour notes could be sulphur containing materials. These are mainly present within the portions of the oil which were deliberated of the volatiles by distillation up to 98° C / 12 mm Hg and subsequently freed of the crystallised diosphenol 2 (Buchu camphor) by low temperature filtration. The filtrate was once again distilled under high vacuum and yielded a residue (5% of the total amount of Buchu Oil used) which was chromatographed on Silica gel.

After a series of sesquiterpene hydrocarbons, an interesting odorous mixture was eluted by hexane/ether (19:1). This fraction contained among others 3 main components in the gaschromatogram [6]. Corresponding GLC-MS coupling experiments [7] allowed us to assign the structure of Ψ-diosphenol 1 [3] and diosphenol 2 [2,8] to two of them. The third main component showed a molecular ion peak at m/e = 186, together with fragment ion peaks at m/e = 75 and 153. These pointed to molecular fragments containing sulphur, because of the positive evidence (test with sodium nitroprusside) for its presence in the chromatographic fraction in question. Hence, a possible elementary composition of $C_{10}H_{18}OS$ for the third main component was advanced as working hypothesis.



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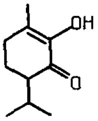

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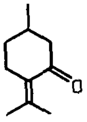

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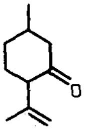

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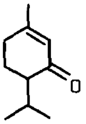
Certain considerations lead us to the assumption that the structure in question could formally be derived from pulegone 3 which is present in the oil (or eventually also from isopulegone 4 or even piperitone 5), by addition of hydrogen sulfide to the C=C double bound. Piperitone 5 was also considered because piperitonepoxide 6 is described by E. Klein et al. [4] to be a main constituent of Buchu Leaf Oil.



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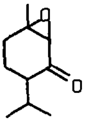

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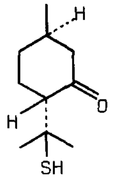
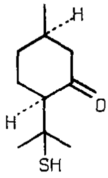
The H_2S adducts of 3, 4, and 5 were therefore prepared using H_2S in a basic medium (KOH/ethanol or triethylamine). Pulegone 3 as well as isopulegone 4 yielded a mixture of two stereoisomeric p-menthane-8-thiol-3-ones; 7 and 8 (b.p. 62°/0,1 mm Hg, n_D^{20}: 1.4948 - 1.4951) in a ratio 3:1 in the case of 3 and about 3:2 in the case of 4, provided that the reaction is executed in an autoclave in presence of KOH/EtOH at 50° C for 2 hours.

The two diastereomers 7 and 8 obtained from dextrorotary pulegone 3 [9] were separated by preparative gas chromatography [10]. They exhibit the following physicochemical properties:

	 7	 8
IR	ν in cm^{-1}	
	2584 (w-m), 1710 (st), 1454 (m), 1384 (w), 1365 (m), 1202 (m), 1140 (w-m), 1122 (w-m), 1048 (w)	2590 (w), 1714 (st), 1470 (w-m), 1385 (m), 1368 (w), 1230 (w), 1140 (w-m), 1122 (m), 1072 (w-m)
NMR	δ in ppm with TMS as internal standard (60 MHz)	
	1,03 (3H, badly resolved doublet traces of pulegone?) 1,45 + 1,485 (6H, 2s) 1,55 - 2,65 (9H, m)	0,96 (3H, d, J = 7 cps) 1,43 + 1,49 (6H, 2s) 1,7 - 2,7 (9H, m)
MS	m/e at 70 eV; peaks in order of decreasing intensity	
	69 (base peak = 100), 41, 112, 109, 186 (M^+), 153, 75	69 (base peak = 100), 112, 186 (M^+), 109, 153, 41, 75
$[\alpha]_D^{20}$	- 32° (c = 0,117 g/dl, MeOH)	+ 40° (c = 0,127 g/dl, MeOH)

The trans-configuration may be assigned to the more abundant, thermodynamically more stable isomer 7.

Processing of a larger quantity of Buchu Leaf Oil was necessary for the preparative isolation of the compounds in question. Thereby it could be shown that p-menthane-8-thiol-3-one found in quantities of equal or less than 0,5% within the Buchu Leaf Oil is also present in the two diastereomeric forms.

The isolated, natural diastereomeric 7:3 mixture shows identical IR, NMR, and MS spectra as well as identical GLC-retention times on polar and apolar stationary phases as an especially prepared synthetic mixture of 7 and 8 in the same ratio. In addition, the mass spectra of the two natural isomers determined by GLC-MS coupling experiments were identical (especially also with respect to characteristic intensity differences of fragment ion peaks at m/e = 109 and m/e = 112) with the corresponding synthetic diastereomeric p-menthane-8-thiol-3-ones 7 and 8.

Under the assumption that the natural p-menthane-thiol-ones are formed formally from (-) pulegone present to about 11% [4] in Buchu Leaf Oil, we can assign them the opposite absolute configuration as the one depicted in formulae 7 and 8.

References

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Guenther, The Essential Oils, Vol. 3, p. 368

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[5] Supplier: White, Tomkins & Courage, Reigate

[6] 2% Carbowax 20 M on Chromosorb G 80/100 mesh, 180° C

[7] Capillary column Triton-X 305 (150° C) coupled to a CEC 21-110 B mass spectrometer

[8] F.W. Semmler et al., Ber.dtsch.chem.Ges. 39, 1158 (1906)

[9] K. Freudenberg, W. Hohmann, Liebigs Ann.Chem. 584, 54 (1953)

[10] 5 to 10% Carbowax 20 M on Chromosorb G 80/100 mesh, 3,6 m length, 15 mm i.d. 180° C.