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J. Nat. Prod., **1993**, 56 (2), 272-274 • DOI:
10.1021/np50092a013 • Publication Date (Web): 01 July 2004

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β -BISABOLENOL AND β -BISABOLENAL, TWO NEW BISABOLENE SESQUITERPENES FROM *NEOCALLITROPSIS PANCHERI*

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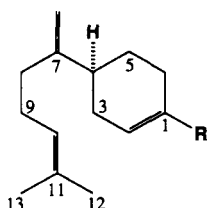
ABSTRACT.—The wood of *Neocallitropsis pancheri* was found to contain two new bisabolene sesquiterpenes, which were identified as 1-hydroxymethyl-4-(5'-methyl-1'-methylene-4'-hexenyl)-cyclohexene [**1**] and 1-carboxaldehyde-4-(5'-methyl-1'-methylene-4'-hexenyl)-cyclohexene [**2**] by ^1H -, ^{13}C - and 2D nmr experiments.

Neocallitropsis pancheri (Carrière) de Laubenfels (Cupressaceae) is an endemic tree which grows in the south part of New Caledonia (1,2). Earlier work on the wood essential oil yielded numerous sesquiterpene alcohols (3–7). As a part of our research program on the phytochemical and physicochemical studies on *N. pancheri*, we have now isolated two new bisabolene sesquiterpenes, β -bisabolol [**1**] and β -bisabolal [**2**]. Their structures were established as 1-hydroxymethyl-4-(5'-methyl-1'-methylene-4'-hexenyl)-cyclohexene [**1**] and 1-carboxaldehyde-4-(5'-methyl-1'-methylene-4'-hexenyl)-cyclohexene [**2**] on the basis of 1D and 2D nmr spectral data.

The molecular formula for β -bisabolol [**1**] [oil, $[\alpha]^{25}_{\text{D}} - 52^\circ$ (CHCl_3 , $c = 0.31$)] was established as $\text{C}_{15}\text{H}_{24}\text{O}$ by eims. Its ir spectrum showed a hydroxyl

group (3659 cm^{-1}) and a C-C double bond (1638 cm^{-1}). ^{13}C proton-noise decoupled and DEPT (8) spectra suggested the bisabolane carbon skeleton for **1** (9). The structure determination for **1** followed from the 2D INADEQUATE experiments (10, 11). From the auto-correlated 2D diagram, all the carbon-carbon connectivities and, therefore, the structure of β -bisabolol were unambiguously established. Complete ^{13}C -nmr assignments are given in Table 1 with the proton assignments obtained from the concerted use of 2D homonuclear (12, 13) and heteronuclear (14, 15) chemical shift correlation techniques. Although the majority of the ^1H signals are found in an unresolved envelope, it was possible to assign the entire proton spectrum from the slices of the chemical shift heteronuclear correlation diagram. One-bond carbon-carbon coupling constants determined from the double quantum coherence spectrum of **1** are presented in Figure 1.

The molecular formula for β -bisabolal [**2**] [oil, $[\alpha]^{25}_{\text{D}} - 45^\circ$ (CHCl_3 , $c = 0.28$)] was found to be $\text{C}_{15}\text{H}_{22}\text{O}$ by eims. The ir spectrum showed a carbonyl absorption band at 1707 cm^{-1} . The ^1H - and ^{13}C -nmr spectral data of β -bisabolal (Table 1) were consistent with a



- 1** R = CH_2OH
2 R = CHO
3 R = Me

TABLE 1. ^1H - and ^{13}C -nmr Chemical Shift^a Assignments for β -Bisabolanol [1] and β -Bisabolenal [2].

Position	Compound					
	1			2		
	Group ^b	$^1\text{H}^c$	$^{13}\text{C}^{c,d}$	Group ^b	$^1\text{H}^c$	$^{13}\text{C}^c$
1	C	—	137.17	C	—	141.33
2	CH	5.65	122.45	CH	6.80	150.84
3	CH ₂	2.12 and 1.88	31.03	CH ₂		32.40
4	CH	2.08	39.88	CH		39.53
5	CH ₂	1.82 and 1.42	27.90	CH ₂		26.78
6	CH ₂	2.04	26.81	CH ₂		21.79
7	C	—	153.81	C	—	152.60
8	CH ₂	2.01	34.85	CH ₂		34.80
9	CH ₂	2.06	26.26	CH ₂		26.83
10	CH	5.05	124.23	CH	5.09	124.01
11	C	—	131.49	C	—	131.89
12	Me	1.63	25.65	Me	1.66	25.75
13	Me	1.55	17.69	Me	1.59	17.80
14	CH ₂	3.95	67.00	CH	9.41	193.99
15	CH ₂	4.70	107.37	CH ₂	4.79 and 4.76	108.25

^aIn ppm from TMS in CDCl₃.

^bDetermined from DEPT spectra.

^cInformation obtained from concerted application of homonuclear and heteronuclear chemical shift correlations.

^dInformation obtained from double quantum coherence measurements.

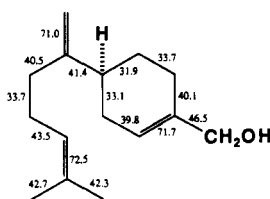


FIGURE 1. Natural-abundance one-bond ^{13}C - ^{13}C coupling constants (in Hz) in **1**, determined from double quantum coherence measurements.

bisabolene structure in which the aldehyde function was present at 9.41 ppm (^1H) and 193.99 ppm (^{13}C). The location of the aldehyde group was determined on the basis of a ^1H - ^1H homonuclear chemical shift correlation experiment. The carbonyl position was further supported by the correlation peak observed between H-2 and the aldehyde resonances in the 2D diagram. Deshielding of the C-2 resonance was also consistent with this structure **2**. Fi-

nally, β -bisabolanol and β -bisabolenal exhibited ^{13}C -nmr spectral parameters similar to those of β -bisabolene [**3**] (**8**) and related products (**16**). Since the optical rotations of **1** and **2** both showed negative values, as for ($-$)- β -bisabolene [**3**] (**17**), we presume the same stereochemistry at C-4 for all three compounds.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Optical rotations $[\alpha]^{25\text{D}}$ were measured on a Perkin-Elmer model 241 polarimeter. Ms were determined on 5970 HP spectrometer. Ir spectra were obtained on 5965 HP apparatus. A 5890 HP gas chromatograph equipped with an FID and a fused Si capillary column [HP-1, 100% dimethyl polysiloxane, 50 m \times 0.32 mm (i.d.), Hewlett-Packard] was used in this work. All nmr spectra were recorded on a Bruker AM 400 X spectrometer; TMS was used as standard in ^1H and ^{13}C measurements. Standard Bruker pulse sequences were used for homonuclear, heteronuclear, and double quantum coherence correlation experiments. For other experimental details see Faure *et al.* (18).

FRACTIONATION AND ISOLATION.—*N. pan-*

cheri, collected in November 1990 as dried wood pieces in the "Montagne des Sources" area in New Caledonia, was identified and cleaned before extraction. A voucher specimen (no. P-R-04-01) is deposited in the laboratoire C2A, Centre Universitaire de Polynésie Française.

N. pancheri heartwood (1005 g) cut in small pieces was steam-distilled (20 h), yielding 102.8 g of viscous yellow essential oil (9.8%). The *N. pancheri* essential oil (4 g) was separated on SiO₂ coated with 10% of AgNO₃ using a stepwise gradient system (toluene to EtOAc).

Fractions of 15 ml were collected and analyzed by gc. Repeated cc (SiO₂/AgNO₃) was carried out to obtain amounts sufficient for structural determination.

Fractions 20–26 eluted with toluene-EtOAc (35:65) were taken to dryness and distilled under vacuum, and gave the major compound **1** (301 mg) as an oil: [α]_D²⁵ -52° (CHCl₃, *c* = 0.31); ν max cm⁻¹ 3659 (OH), 1638 (C=C); ms *m/z* (% rel. int.) [M]⁺ 220 (7.3), 189 (9.2), 177 (8.5), 135 (9.6), 109 (27.2), 93 (35.7), 77 (29.8), 69 (100), 41 (92.1); ¹H and ¹³C nmr see Table 1.

Fractions 6–11 eluted with toluene-EtOAc (60:40) were taken to dryness and purified by additional Si gel cc (CH₂Cl₂), and gave compound **2** (112 mg) as an oil: [α]_D²⁵ -45° (CHCl₃, *c* = 0.28); ν max cm⁻¹ 1707 (α,β -unsaturated C=O); ms *m/z* (% rel. int.) [M]⁺ 218 (7.5), 175 (29.5), 147 (5.4), 135 (9.7), 109 (47.2), 91 (18.7), 77 (21.4), 69 (100), 41 (86.7); ¹H and ¹³C nmr see Table 1.

ACKNOWLEDGMENTS

We are grateful to Mr. M Point for his help in collecting the plant material and Mr. G. George, Sanofi BioIndustries, for helpful discussions.

LITERATURE CITED

1. R.H. Compton, *J. Linn. Soc.*, **14**, 432 (1922).
2. D.J. De Laubenfels, "Flore de la Nouvelle-Calédonie et Dépendances," Muséum National d'Histoire Naturelle, Paris, 1972, Vol. 4, p. 161.
3. E. Guenther, "The Essential Oils," D. Van Nostrand Company, New York, 1952, Vol. VI, p. 321.
4. S. Arctander, "Perfume and Flavor Materials of Natural Origin," Author, Elizabeth, New Jersey, 1960, p. 71.
5. E. Von Rudloff, *Chem. Ind. (London)*, 743 (1962).
6. R.B. Bates and E.K. Hendrickson, *Chem. Ind. (London)*, 1759 (1962).
7. E. Von Rudloff, *Chem. Ind. (London)*, 211 (1964).
8. D.M. Doddrell, D.T. Pegg and M.R. Bendall, *J. Magn. Reson.*, **48**, 323 (1982).
9. H.O. Kalinowski, S. Berger, and S. Braun, "Carbon-13 Nmr Spectroscopy," J. Wiley & Sons, New York, 1988, p. 433.
10. A. Bax, R. Freeman, and T.A. Frenkiel, *J. Am. Chem. Soc.*, **103**, 2102 (1981).
11. A. Bax, R. Freeman, T.A. Frenkiel, and M.H. Levitt, *J. Magn. Reson.*, **43**, 478 (1981).
12. K. Nagayama, A. Kumar, K. Wüthrich, and R.R. Ernst, *J. Magn. Reson.*, **40**, 321 (1980).
13. R. Freeman, G.A. Morris, and A. Bax, *J. Magn. Reson.*, **42**, 164 (1981).
14. A.A. Maudsley and R.R. Ernst, *Chem. Phys. Lett.*, **50**, 368 (1977).
15. G. Bodenhausen and R. Freeman, *J. Am. Chem. Soc.*, **100**, 320 (1978).
16. J.S. Mossa, I. Muhammad, F.S. El-Ferally, C.D. Hufford, D.R. McPhail, and A.T. McPhail, *Phytochemistry*, **31**, 575 (1992).
17. Y.R. Naves and P. Ardizio, *Bull. Soc. Chim. Fr.*, 334 (1954).
18. R. Faure, A.R. Ramanoelina, O. Rakotonirainy, J.P. Bianchini, and E.M. Gaydou, *Magn. Reson. Chem.*, **29**, 969 (1991), and references cited therein.

Received 25 May 1992