Phytochemistry, Vol. 21, No. 4, pp. 937–938, 1982.
Printed in Great Britain.

0031-9422/82/040937-02$03.00/0
Pergamon Press Ltd.

SHORT REPORTS

STRUCTURE ANALYSIS OF PROXIMADIOL (CRYPTOMERIDIOL) BY ^{13}C NMR SPECTROSCOPY*

FREDERICK E. EVANS, DWIGHT W. MILLER, THOMAS CAIRNS,† G. VERNON BADDELEY‡ and ERNEST WENKERT‡

National Center for Toxicological Research, Jefferson, AK 72079, U.S.A.; ‡Department of Chemistry (D-006), University of California, San Diego, La Jolla, CA 92093, U.S.A.

(*Received* 23 *February* 1981)

Key Word Index—*Cymbopogon proximus*; Gramineae; sesquiterpene diol; proximadiol; cryptomeridiol.

Abstract—The sesquiterpene diol with antispasmodic properties, earlier isolated from *Cymbopogon proximus*, is shown to be identical with cryptomeridiol.

INTRODUCTION

The Egyptian desert weed *Cymbopogon proximus* Stapf has been shown to contain a bicyclic sesquiterpene diol, proximadiol, with unique antispasmodic properties [1]. The present structure analysis reveals the bioactive principle to be identical with cryptomeridiol [2, 3], a sesquiterpene of the eudesmane type (**1**).

RESULTS AND DISCUSSION

The ^{13}C NMR chemical shifts and related multiplicities in the offresonance decoupled spectra were in accord with structure **2** for proximadiol. Shift assignments were made through shift comparison with β-eudesmol (**3**) [4] and isointermedeol (**4**) [5] and with a limited number of carbons of heterocladol [6] and (1*S*)-bromo-(4*R*)-hydroxy-(−)-selin-7-ene [7], in as a consequence of the absence of a C-7 axial substituent.

Shift assignments of the carbons of the second ring and the side-chain followed from those for β-eudesmol (**3**) and isointermedeol (**4**). In comparison with the first model, C-6 of proximadiol displays additional shielding from the C-4 substituents. In the absence of an axial C-7 substituent, C-9 of proximadiol is deshielded compared to the second model. It is noteworthy that the introduction of a 4β-substituent into an angularly methylated *trans*-decalin skeleton order to establish the relative stereochemistry of the new terpene alcohol.

Shifts were assigned to sites in the hydroxylated ring by analogy with those for isointermedeol (**4**), possessing an equatorial hydroxyl group at C-4. A reversal of the stereochemistry at C-4 leads to a low-field methyl resonance, as seen at δ 29.6 in (1*S*)-bromo-(4*R*)-hydroxy-(−)-selin-7-ene [7] and at 35.7 in heterocladol [6], in which one γ-interaction with C-6 is lacking. In comparison with isointermedeol (**4**) C-5 of proximadiol is deshielded by δ 5.7 deshields C-9 by *ca* δ 3, as illustrated by the $\Delta\ \delta$ values for the corresponding carbon in the following three pairs of compounds: (a) *trans*-9-methyldecalin and *trans*-1,1,10-trimethyldecalin [8]; (b) β-eudesmol (**3**) and proximadiol (**2**); (c) the C-4 epimers of 4,14-dihydro-β-eudesmol [9]. In the latter case the chemical shifts assigned to C-1 and the 4-methyl group of the 4β-methyl isomer require interchange with those of C-9 and the C-10 methyl group, respectively.

Selective decoupling of the hydrogens of the methyl groups attached to the oxycarbons of proximadiol allowed the oxycarbon shifts to be distinguished.

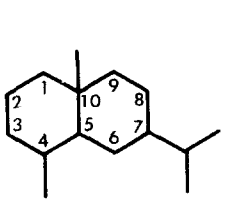
The above data define the relative stereochemistry of proximadiol as depicted in formula **2**. Since this configuration was assigned previously to cryptomeridiol [2, 3], the physical properties of the two compounds were compared and the substances shown to be identical.

EXPERIMENTAL

The ^{13}C NMR spectra were determined at room temp. on $CDCl_3$ solns of proximadiol and cryptomeridiol. The chemical shifts of proximadiol are reported in ppm downfield from internal TMS and those depicted on formulae **3** and **4** are taken from the literature. The starred δ values may be interchanged. The ^1H NMR [δ 0.86, (3H, *s*), 1.12 (3H, *s*), 1.21 (6H, *s*)] and MS data were in agreement with those reported for cryptomeridiol [2, 3]. Co-chromatography (4 ft × 2 mm i.d. 3% SP 2250 glass column, 150°, 30 ml/min He flow rate) of proximadiol and cryptomeridiol gave a

*Part 74 in the series "Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances". For Part 73, see Wenkert, E., Halls, T. D. J., Ceccherelli, P., Curini, M. and Pellicciari, R. (1981) *J. Org. Chem.* **46**, 3135. Part 2 in the series "Structure Analysis of Complex Bioorganic Molecules by Nuclear Magnetic Resonance Spectroscopy". For Part 1, see Evans, F. E., Fu, P. P., Cairns, T. and Yang, S. K. (1981) *Analyt. Chem.* **53**, 558.

†Present address: Food and Drug Administration, FDA District Office, 1521 West Pico Blvd., Los Angeles, CA 90052, U.S.A.



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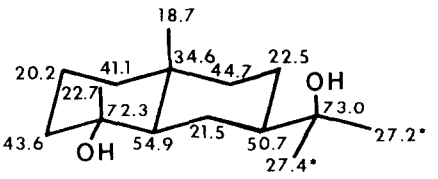

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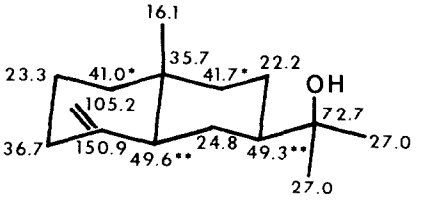

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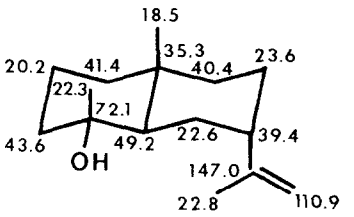

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single retention time of 15.8 min. The specific rotation of proximadiol, $[\alpha]_D^{23} - 26°$ ($CHCl_3$; *c* 2.0) was in agreement with that of cryptomeridiol [2].

Acknowledgements—The authors are indebted to Drs. Amir Girgis, National Organization for Drug Control and Research, Giza, Egypt, and G. Ohloff, Firmenich SA, Geneva, Switzerland, for gifts of samples of proximadiol and cryptomeridiol, respectively, to Professor E. J. Eisenbraun, Oklahoma State University, Stillwater, OK 74074, U.S.A., for the optical rotation determinations and to Drs. J. P. Freeman and R. K. Mitchum (NCTR) for the GC–MS analysis.

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