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## CONCERNING MONTBRETYL 12-METHYL ETHER

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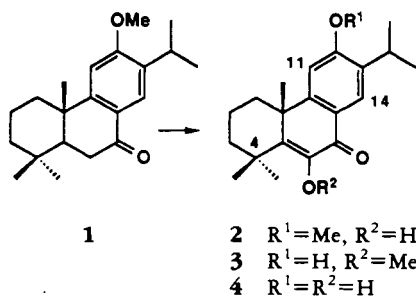
ABSTRACT.—The structure **2** proposed for montbretyl 12-methyl ether is shown to be incorrect by unambiguous synthesis.

Recently Ulubelen and Topcu (1) suggested structure **2** for a diterpene they isolated from *Salvis montbretii* collected in Turkey. In another context, we have prepared (2) this structure from sugiol methyl ether [**1**]. The latter had been synthesized from podocarpic acid by known transformations (3). Oxygenation of **1** in *t*-BuOK/*t*-BuOH afforded **2**. We have repeated this preparation to obtain more recent data only to confirm our suspicion that the synthetic product showed significant spectroscopic differences with the reported natural substance (Scheme 1).

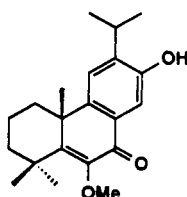
The crucial ir band for the hydroxyl-chelated and conjugated aromatic ketone which appears at  $1615\text{ cm}^{-1}$  in the synthetic compound is given as  $1665\text{ cm}^{-1}$  for the natural product. There are other major differences in the  $^1\text{H}$  nmr, including 4,4-dimethyls at  $\delta$  1.43 and 1.46 (natural product  $\delta$  1.28), the 10-Me at  $\delta$  1.53 (natural product  $\delta$  1.67), and aromatic protons H-11 and H-14 at  $\delta$  6.86 and 7.96 (natural product  $\delta$  6.48 and 7.73), and in the  $^{13}\text{C}$  nmr the resonances at  $\delta$  179.7 (C-7), 154.8 (C-9), 161.1 (C-12), 136.3 (C-13), 124.6 (C-14), and 55.4 (12-OMe) differ greatly

from the values  $\delta$  185.4, 148.8, 152.3, 130.8, 117.7, and 57.5 given for the natural product. It would be tempting to suggest that the montbretyl 12-methyl ether described is in reality the 6-methyl ether **3**, since methylation of the enolic hydroxyl would move the carbonyl band to higher frequency in the ir [typically  $20\text{--}30\text{ cm}^{-1}$ ; see examples in Burnell and co-workers (3,4)], but the H-14 signal in the nmr would still be too low (typically ca.  $\delta$  8.0). It should be added that the  $^{13}\text{C}$ -nmr resonance of a 12-OMe rarely falls outside the range of  $\delta$  55–56 unless C-11 also bears an hydroxyl or a methoxyl [see Burnell *et al.* (4) for examples].

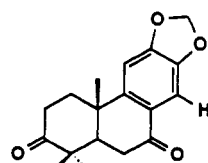
This makes proposing a structure for the natural product difficult, but **5**, which contains the corresponding functional groups on the semperviroil skeleton, looks feasible. The 13-OH would shield H-14 to a relative upfield resonance as illustrated by the  $\delta$  7.43 signal for this proton in the spectrum of **6** (5). We cannot comment on the structure proposed for montbretol [**4**], but the great similarity of its spectral properties suggests that it too should be modified. Unfortunately in our hands attempted demethylation of synthetic **2** ( $\text{BBr}_3$ ,  $\text{CH}_2\text{Cl}_2$ ) led to considerable decomposition.



SCHEME 1



5



6

## EXPERIMENTAL

12-METHOXY-6-HYDROXYABIETA-5,8,11,13-TETRAEN-7-ONE [2].—Sugiol methyl ether [1] (91 mg) was added to *t*-BuOH (15 ml) containing *t*-BuOK (2.10 g). At room temperature, oxygen was slowly bubbled through the solution for 2 h, after which the mixture was poured into 10% aqueous HCl and the Et<sub>2</sub>O extracted. The residue was flash-chromatographed over Si gel [petroleum ether-Et<sub>2</sub>O (4:1)], affording the usual lactol (22 mg) resulting from subsequent oxidation (6) and the diosphenol 2 (49 mg, 52%): mp 144–146°; [α]<sup>25</sup><sub>D</sub> 17.13 (*c* = 1.0, CHCl<sub>3</sub>); ir (CHCl<sub>3</sub>) 3335, 1622, 1595, 1490, 1242, 1163, 1045 cm<sup>-1</sup>; <sup>1</sup>H nmr δ (CDCl<sub>3</sub>) 1.23 and 1.26 (2d, 3H ea, *J* = 7 Hz, *i*Pr Me), 1.43 (s, 6H, 4,4-diMe), 1.53 (s, 3H, 10-Me), 3.28 (sept, 1H, *J* = 7 Hz, *i*Pr CH), 3.90 (s, 3H, 12-OMe), 6.86 (s, H-11), 7.17 (s, OH), 7.98 (s, 1H, H-14); <sup>13</sup>C nmr δ (C-1 to C-20) 35.9, 17.6, 33.7, 37.8, 143.8, 140.6, 179.7, 120.5, 154.8, 40.6, 106.0, 161.1, 136.3, 124.6, 26.6, 22.6, 22.4, 28.1, 27.8, 35.1, 55.4 (12-OMe); ms *m/z* [M]<sup>+</sup> 328 (100), 313 (15), 285 (24), 259 (59), 258 (54),

243 (16), 217 (54). *Anal.* calcd for C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>: C 76.79, H 8.59; found C 76.97, H 8.51.

## ACKNOWLEDGMENTS

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## ERRATUM

For the paper by Boonyaratavej *et al.* entitled "trans-Triacontyl-4-hydroxy-3-methoxycinnamate, a New Compound from the Thai Plant *Bridelia ovata*," *J. Nat. Prod.* **55**, 1761 (1992), the title compound is not novel to the natural product literature. It has been previously reported using ms and gc in a mixture of ferulate esters of higher fatty alcohols obtained from the roots of *Kalanchoë daigremontiana* [Nair *et al.*, *J. Chem. Ecol.*, **14**, 589 (1988)].