

## ERRATUM

The authors wish to make the following corrections to their paper which appeared in *Journal of Labelled Compounds and Radiopharmaceuticals*, Vol XLI, No. 1, pp 63-74 (1998).

Xiangdong Su, Abdul Siddiqui, Shankar Swaminathan, William K. Wilson, and George J. Schroepfer, Jr.\* PREPARATION OF 25,26,26,26,27,27,27-HEPTAFLUORO-15-KETOSTEROLS LABELED AT C-23 WITH DEUTERIUM OR TRITIUM

Our error in matching the  $^2\text{H}$  NMR signals with corresponding C-23 proton signals of known stereochemical assignment led to a reversal of designations for deuterium at the 23*R* and 23*S* positions. Correction of this error requires the following changes:

Figure 2 and its legend should be replaced by the following:

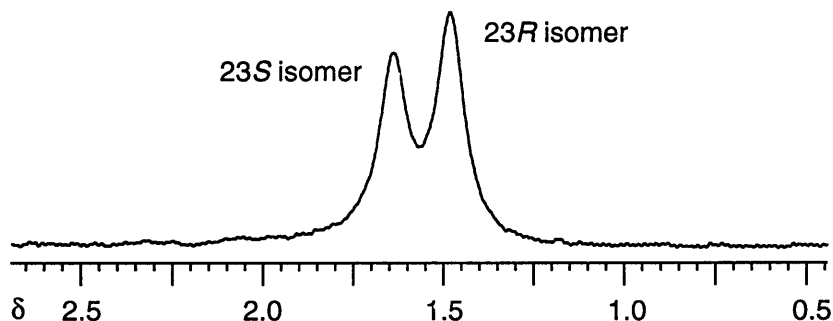


Figure 2.  $^2\text{H}$  NMR spectrum of F<sub>7</sub>-15-ketosterol [ $^2\text{H}$ ]-2, which is a 5:4 mixture of the 23*R*- and 23*S*-deuterio isomers. Assignment of stereochemistry is based upon  $^1\text{H}$  NMR signal assignments established by us for the side-chain protons of F<sub>7</sub>-15-ketosterols (2, 3, 5).

In the sentence introducing Figure 2 (page 65, para. 2, lines 6-8), 23*S* should be changed to 23*R*.

The last paragraph beginning on page 67 should be replaced by the following:

The free radical mechanism normally observed for tributyltin hydride reductions of alkyl halides leads to loss of any existing stereochemical identity at the central carbon atom (12). Any stereoselectivity (observable in reductions with tributyltin deuteride) is attributable to steric differences in the approach of the tributyltin hydride to the radical center (11, 13). As noted above,  $^2\text{H}$  NMR analysis of the deuterated sterols indicated a slight preference (5:4 or 3:2 ratio) for the 23*R*-deuterio epimers over the 23*S* products (14). Interestingly, formation of the 23-iodides by free-radical addition of heptafluoroisopropyl iodide to a  $\text{C}_{24}\text{-}\Delta^{23}$  steroid, gave a much higher ratio (6:1) of the 23*R*- to 23*S* iodides. These strikingly different results might be attributable simply to differences in steric requirements between heptafluoroisopropyl iodide and tributyltin deuteride. A more plausible explanation is that formation of the 23*R* isomer is slightly favored kinetically in both reactions but the reaction is reversible only in the case of the iodide. Thus, tributyltin deuteride reduction gives the kinetic product (slightly favoring 23*R* over 23*S*) whereas the iodide addition reaction is reversible and affords a mixture resembling the thermodynamic product (strongly favoring 23*R* over 23*S*). In support of this explanation, we have previously suggested that the iodide addition reaction is reversible (5) and that the best conformations of the 23*S*-iodides have unfavorable *gauche* interactions not present in the prevailing side-chain conformation of the 23*R*-iodide (2).

The following text should be added to Footnote 14:

The slight preference for 23*R*-deuterio epimers in the tributyltin deuteride reductions of F<sub>7-15</sub>-ketosterols is attributable to partial blockage of the *Si* face by the C-20 methyl group in the extended conformation of the radical intermediate. Other considerations include blockage by the trifluoromethyl groups at C-25 (affecting attack on the *Re* and *Si* faces approximately equally), the significant population of the +*gauche* C17-C20-C22-C23 rotamer (favoring attack on the *Re* face), and increased conformational heterogeneity in the vicinity of the C-23 radical center (probably decreasing stereoselectivity). Attack by either deuterio or iodo species on the *Re* face gives the 23*R* isomer.

Designations of 23*R* and 23*S* should be reversed in descriptions of  $^2\text{H}$  NMR data on pages 69-71. For example, for compound [ $^2\text{H}$ ]-6 on page 69:

5:4 ratio of singlets at  $\delta$  1.48 (H-23*S*) and 1.64 (H-23*R*)

should be replaced by

5:4 ratio of singlets at  $\delta$  1.48 ( $^2\text{H}$ -23*R*) and 1.64 ( $^2\text{H}$ -23*S*).