

FARADIOL AND ARNIDIOL - REVISION OF THE STRUCTURE

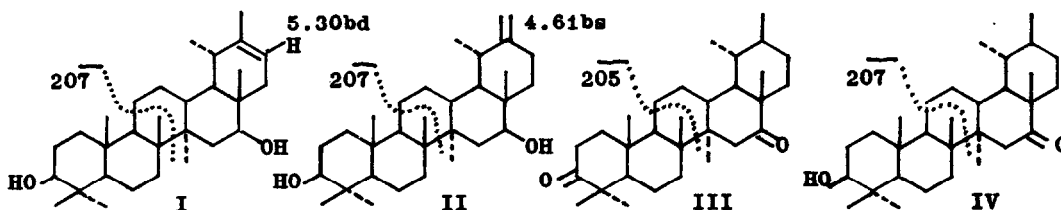
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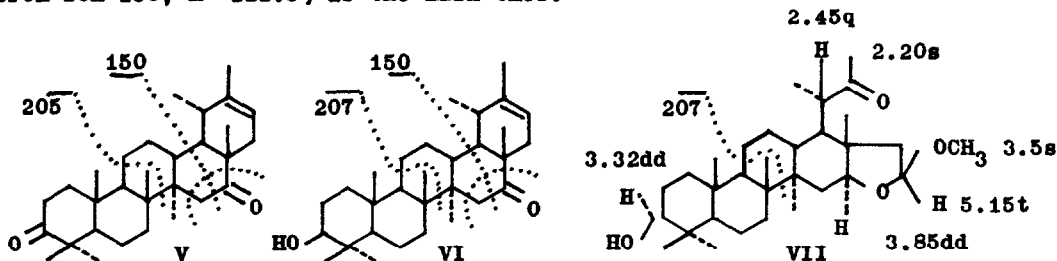
Faradiol and arnidiol are two main triterpenes occurring in yellow Compositae flowers (Arnica, Calendula, Helianthus, Taraxacum, Tussilago and Senecio)¹. Based on degradation of their common derivative - dihydrofaradione - positions of the hydroxyl groups were established to be 3 and 12².

The subject of this paper is the reexamination of faradiol structure, which showed that faradiol is 3 β ,16 β -dihydroxy- Ψ -taraxene I³. Arnidiol, in contrast to the previous data^{1,2}, differs only in the position of the double bond and has the structure of 3 β ,16 β -dihydroxytaraxene II.



Oxidation of dihydrofaradiol (m.p. 245-246°, $[\alpha]_D^{20} 0^{04}$) with one equivalent of CrO_3 led to dihydrofaradione III (m.p. 182-185°, $[\alpha]_D^{20} -18^0$ and 3 β -hydroxy-16-ketotaraxastane IV (m.p. 235-237°, $[\alpha]_D^{20} -50^0$)⁵. The latter one was reduced by Wolff-Kizner method to taraxastanol (m.p. 223-225°, $[\alpha]_D^{20} +3.5^0$). In the pmr spectra of both ketones III and IV C-15 methylene group signal is clearly visible as AB quarted ($J=14.5$ Hz, δ 15 α H 1.88, δ 15 β H 2.85 little broadened). In the spectrum of III also C-2 methylene group signal is present (multiplet δ 2.45). Dihydrofaradione III equilibrated with refluxing $\text{D}_2\text{O}/\text{NaOD}/\text{diglime}$ (m.p. 183-185°) incorporated four deuterium atoms, the molecular ion being shifted from 440 to 444 m/e for the oxygen positions 3 and 12 five protons

should be exchanged), and from its pmr spectrum the signals of four above mentioned protons disappeared completely. The only significant fragmentation process in the mass spectra of saturated ketones III and IV is the formation of "AB" fragment, as in the case of Ψ -taraxasterol⁶ and Ψ -taraxastene (207 and 191 resp.). Unsaturated ketones: faradiolone V (m.p. 245°) and 3 β -hydroxy-16-keto- Ψ -taraxene VI (m.p. 225-227°, $[\alpha]_D -20^\circ$, transformed to Ψ -taraxasterol by Wolff-Kizner reduction) along with the above process, exhibited the elimination of 43 m/e (C₂H₃O by H.R.), 149 (C₁₀H₁₃O by H.R.), 150 (C₁₀H₁₄O by H.R.) and 135 (from ion 150, M^x 121.5) as the main ones.



Unambiguous proof of the 16 β position for the second hydroxyl group was obtained by OsO₄/KIO₄ oxidation of faradiol I. Treatment of the product with hot methanol formed the acetal VII in good yield (m.p. 210°, $\nu_{\text{max}}^{\text{KBr}}$ 1700 cm⁻¹, ms: 488 M⁺, 470, 456... 207, 189...). Its pmr spectrum shows the presence of one methoxyl group, one acetyl group and other acetal ring protons.

Arnidiol II diacetate obtained from natural diol mixtures (m.p. 189°, $[\alpha]_D +79^\circ$) showed in the pmr spectrum the same two double doublets as faradiol I diacetate (m.p. 163°, $[\alpha]_D +54^\circ$) with coupling constants typical for equatorially located secondary hydroxyl groups: 3 α H δ 4.60 J=9 and 7 Hz, 16 α H δ 4.83 J=11 and 5 Hz.

We are very grateful to Prof. M. Kocór for fruitful discussions.

References and notes:

1. "Elsevier Encyclopedia of Organic Chemistry", Vol. 14 Supplement, 1163,
2. J. O. Santer and R. Stevenson, *J. Org. Chem.*, **27**, 3204 (1962),
3. The problem of reassignment of faradiol structure arose in the course of new sunflower triterpene triols structure elucidation.
4. For all substances correct elemental analyses were obtained.
5. The compound described by Santer and Stevenson as 3 β -hydroxy-12-keto-taraxastane m.p. 224-227°, $[\alpha]_D +9^\circ$, should be an 3 α isomer of IV.
6. H. Budzikiewicz, J. M. Wilson and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).