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# CHIEF TERPENOID CONSTITUENTS OF THE *ARTEMISIA SPICATA*

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**Abstract**—The essential oil of *Artemisia spicata* Wulf. contains about 90 per cent of α- and β-thujone; the plant also possesses the sesquiterpene lactone santamarine.

Studies on the terpenoid constituents of aromatic plants growing in Piedmont (Italy),[1–5] have been extended to *Artemisia spicata* Wulf. (*A. genipi* Webb.), whose chemical composition appears not to have been previously examined. This small plant, which grows on the slopes of the Western Alps above 2000 m, is largely used in popular medicine as eupeptic and tonic.

It was not possible to examine fresh plant material and the essential oil was therefore extracted or steam distilled from dried plants collected in two successive years; both methods gave a pale yellow oil with a very agreeable smell, which had practically the same composition, as shown by GLC analysis. The oil contains about 90 per cent α- and β-thujone, which were identified on the basis of their GLC retention data, i.r. spectra and TLC analysis. Other minor components are also present and of these, the most interesting are those components which have high retention times, since they contribute to the characteristic agreeable scent.

The absence of both free and esterified thujilic alcohols was established with certainty[6] and indicates that there is no biogenetic relationship between the thujilic alcohols and the two isomeric thujones.[7–10] Moreover the essential oil does not contain 1,8-cineole, which is present in many other essential oils of the Artemisiae and which has been shown to be biogenetically related to α-thujone in *A. pontica*.[1,2] These facts indicate that the biosynthesis of the two isomeric thujones in *A. spicata* proceeds by pathways other than those mentioned above.

From the alcoholic extract of the dried plant a sesquiterpene ($C_{15}H_{20}O_3$, m.p. 136–138°) was isolated which on the basis of its i.r. and NMR spectra and its chemical and physicochemical behaviour was identified as santamarine (I). This compound belongs to the santanolide (eudesmanolide) group, and was previously isolated from *Chrysanthemum parthenium*

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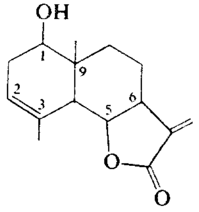
growing on the Mexican plateaux.[11] It is noteworthy that earlier examination of *C. parthenium* showed that it normally contains parthenolide.[12] It would be interesting to see whether *A. spicata* grown at a lower altitude produces santamarine or not.



## EXPERIMENTAL

### *The Essential Oil*

The essential oil was obtained either directly by steam distillation of the dried plant or by extraction with ethanol, concentration and extraction of the oil from the aqueous ethanol with light petroleum, followed by steam distillation. In the latter case the aqueous-alcoholic phase was re-extracted with benzene for the isolation of santamarine.

The essential oil was analysed by GLC using a Perkin–Elmer Model 116 gas chromatograph and the columns K and R at 138 and 180°, respectively. The two major components were collected together and the i.r. spectrum recorded with the Beckman i.r.-5 spectrophotometer in NaCl microcell, thickness 0·1 mm. The spectrum was identical with that of a composite spectrum of pure specimens of α- and β-thujone. The same components were separated on TLC (silica-gel G Merck, 300 μ, activation 15 min at 110–115°)[13] with benzene–methanol (99:1); 10% phosphomolybdic acid solution in ethanol and heating gave two discrete red–violet spots ($R_f$ 0·84 and 0·86) corresponding to α- and β-thujone, respectively.[6]

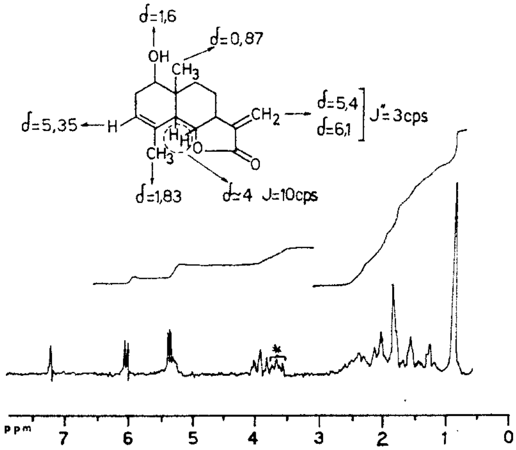


FIG. 1. NMR SPECTRUM OF SANTAMARINE.

Instrument: Varian H-100. Solvent: $CDCl_3$. Internal standard: TMS.

* Signals due to impurities.

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### *Santamarine*

The benzene phase from above was concentrated *in vacuo* and chromatographed on alumina (70 g alumina, grade V Brockmann; column 230×25 mm; eluent, anhydrous benzene). The first 250 ml of eluate were discarded; the next 350 ml of eluate gave, after evaporation of solvent *in vacuo*, a white residue, which after several recrystallizations from ethyl acetate and finally from aqueous-ethanol had m.p. 136–138°. (Found: C, 72·18; H, 8·73; O, 19·07. $C_{15}H_{20}O_3$ required: C, 72·55; H, 8·12; O, 19·33 per cent.)

I.r. spectrum (KBr): free OH at 3400 $cm^{-1}$; unsaturated $\gamma$-lactone at 1773 $cm^{-1}$. NMR spectrum (NMR Spectrometers, Varian A-60 and H-100; solvent $CDCl_3$; internal standard TMS). Doublet at 6·1 and 5·4 ppm (2 H), $J=3$ cps: exocyclic methylene group conjugated with the carbonyl group of lactone; broad singlet at 5·35 ppm (1 H): vinylic hydrogen at $C_3$; singlet at 1·6 ppm (1 H), which disappears after addition of $D_2O$: hydroxyl group at $C_1$; singlets at 0·87 and 1·83 ppm (3 H): two methyl groups at $C_4$ and $C_9$, respectively (Fig. 1).

TLC (silica-gel G Merck, 300 $\mu$, activation 20 min at 115°, eluent benzene, solvent front height 110 mm, development by spraying with 50% sulphuric acid solution in ethanol and heating for 10 min at 110° in oven). Santamarine: $R_f$ 0·27, yellow–orange spot; Artabsine: $R_f$ 0·27, violet spot.

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