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# TRITERPENES XIII(1). SERJANIC ACID, A NEW TRITERPENE FROM THE SAPINDACEAE.

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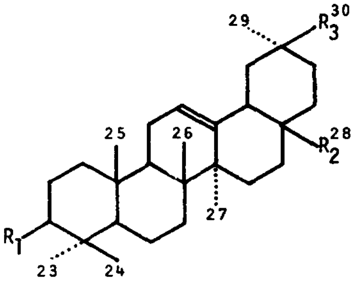
During the 1962 APPA expedition in the Upper Amazon, a *Serjania* sp. (Fam. Sapindaceae) known under the vernacular name "Timbó tres quinas" and locally used as a fish poison was collected near Nova Vida, Territory of Rondonia, Brazil. Pertinent botanical material has been deposited in the Herbarium of the Jardim Botanico, Rio de Janeiro, in order to allow future specific identification.

An alcoholic extract of the plant was submitted to acid hydrolysis and the resulting chloroform-soluble fraction worked up by repeated silicagel column chromatography. This procedure yielded β-sitosterol, large amounts of oleanolic acid and, amongst other minor components, 13 mg of amorphous serjanic acid (I), homogeneous by TLC in various solvent systems. Its NMR spectrum (in pyridine) showed the presence of six tertiary methyl groups and one carbomethoxyl function. Compound I was treated with ethereal diazomethane, yielding methyl serjaniate (II),m.p. 226-229.5°,$(\alpha)_D^{CHCl_3}$ 78°. The 60 Mc NMR spectrum of II in $CDCl_3$ showed six tertiary methyls at 44(3H), 47.5(3H), 55(3H), 60(3H) and 66(6H) cps as well as two carbomethoxyl functions absorbing at 216 and 223 cps (3H each). There was no UV absorption above 210 mμ. IR spectrum (KBr pellet) : broad $\nu_{OH}$ around 3420 $cm^{-1}$ and characteristic absorptions at 1729 (ester $\nu_{C=O}$), 1664 (weak, $\nu_{C=C}$), 1201 (ester $\nu_{C-O}$) and 1026 (alcohol $\nu_{C-O}$) $cm^{-1}$. The mass spectrum contained peaks at *m/e* 514 (corresponding to a molecular ion $C_{32}H_{50}O_5$), 306, 247 (306-COOMe) and 246 (306-COOMe-H). If the peak at *m/e* 306 was to be explained on the basis of a retro Diels-Alder type fragmentation (2), then the above data were compatible with the formulation of compound II as the dimethyl ester of a monohydroxylated triterpene diacid belonging to the $\Delta^{12}$-oleanene group. Both carbomethoxyl groups had then to be on rings D and (or) E, the available positions being C-27, C-28, C-29 and C-30.

Recent data on the influence of substitution on the methyl frequencies in the NMR spectrum of $\Delta^{12}$-oleanene derivatives (3) were applied in order to elaborate a working hypothesis for the structure of methyl serjaniate (II). On biogenetical grounds, it was highly probable that the hydroxyl group was 3β and that one of the carbomethoxyls was in C-28. Neglecting for the time being the influence of the second carbomethoxyl group, the positions of the methyl frequencies of such a compound could be calculated as follows :

| | Me-23 | Me-24 | Me-25 | Me-26 | Me-27 | Me-28 | Me-29 | Me-30 |
|---|---|---|---|---|---|---|---|---|
| Base values : | 53 | 50.5 | 56.5 | 59 | 69 | — | 53 | 53 |
| 3β-OH : | +7 | -2 | +0.5 | +1 | 0 | — | 0 | 0 |
| 28-COOMe : | -0.5 | -0.5 | -1 | -15.5 | 0 | — | +2.5 | +3 |
| Calculated : | 59.5 | 48 | 56 | 44.5 | 69 | — | 55.5 | 56 |
| Observed for II : | 60 | 47.5 | 55 | 44 | 69 | — | 69 | |

Calculated and observed values are in close agreement for methyls 23, 24, 25, 26 and 27. The discrepancy observed for the last methyl group implied that either methyl 29 or 30 was oxidized in -COOMe. It has been previously established $^{(3)}$ that the presence of such a group at C-30 causes a +20 cps frequency shift for the absorption of Me-29. If this were the case one should observe an absorption at 76 cps. The experimental value of 69 cps strongly suggested the reverse arrangement, *i.e.* the location of the carbomethoxyl function at C-30.



**I.** $R_1$=OH ($R_2$=COOH, $R_3$=COOMe) or ($R_2$=COOMe, $R_3$=COOH)
**II.** $R_1$=OH $R_2$=$R_3$=COOMe
**III.** $R_1$=OH $R_2$=$R_3$=$CH_2OH$
**IV.** $R_1$=OH $R_2$=COOH $R_3$=$CH_2OH$

In order to check the validity of the above hypothesis, compound II was reduced with lithium aluminium hydride, yielding serjaniatriol (III), m.p. 268-270°. On the other hand, a sample of queretaroic acid $^{(4)}$(IV), kindly supplied by Dr. Carl Djerassi, was reduced under the same conditions, affording queretaroatriol m.p.269-272°, identical to IV. No depression of the mixed melting point was observed, both compounds had identical mass spectra and were undistinguishable by TLC in various solvent systems. This establishes completely the structure of methyl serjaniate as II, serjanic acid (I) being one of the corresponding monoacid monomethyl esters. The question of the choice between the two existing possibilities remains open.

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