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JURUBINE, A NOVEL TYPE OF STEROIDAL SAPONIN WITH (25S)-3β-AMINO-5α-FUROSTANE-22α.26-DIOL O(26)-β-D-GLUCOPYRANOSIDE STRUCTURE FROM SOLANUM PANICULATUM L. *

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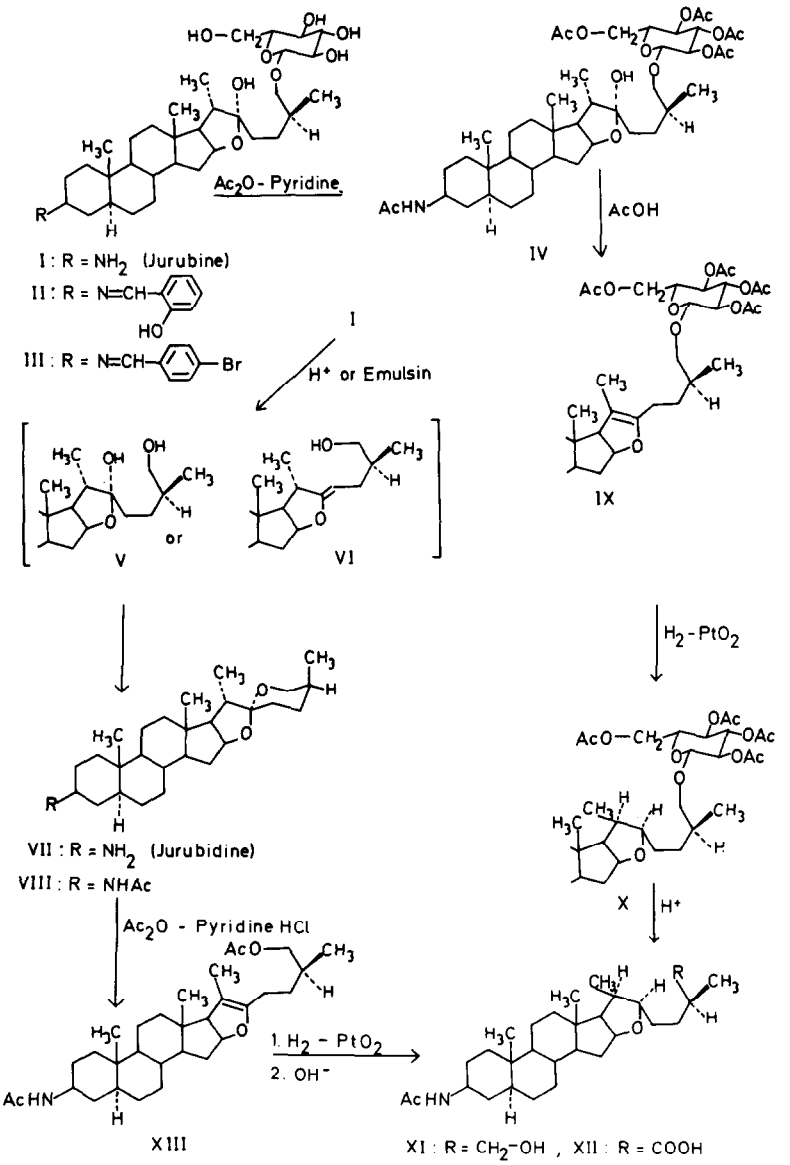
NEARLY twenty years ago, Marker et al. (1) suggested that the true naturally occurring steroidal saponins synthesized by plants might have an open side chain moiety in which ring closure to the spiroketal structure encountered in the corresponding sapogenins is prevented by conjugation of the hydroxy groups at C-16 or C-26 with sugars. According to this hypothesis the spirostane skeleton of the sugar-free sapogenins is thus considered to be an artefact produced by acid hydrolysis of the glycosides, accompanied by cyclization of the intermediate ring E- or F-opened aglycones. Later investigations especially those of Wall et al. (2) could not confirm

* Solanum Alkaloids. Part LXXVIII. - Part LXXVII of this series cf. G. Adam and K. Schreiber, Tetrahedron, in press.

Marker's view and all native saponin preparations examined (2a) showed the same four infrared maxima at about 860, 900, 920, and 980 cm^{-1} as were found to be highly characteristic of the spiroketal side chain in the corresponding sugar-free spirostanes (3). Furthermore, very mild enzymic hydrolysis of the saponins, which was considered to exclude the proton catalysis thought necessary for the cyclization of the initially produced Ring E- or F-opened aglycone to the isolated spirostane yielded the same products as were obtained on acid cleavage (2b).

In contrast to these previous findings (2) and in accord with the former suggestions of Marker (1) we have been able to isolate a nitrogenous steroidal saponin lacking a spiroketal moiety from the roots of the solanaceous plant Solanum paniculatum L., the structure of which has been established as (25S)-3ß-amino-5α-furostane-22α.26-diol O(26)-ß-D-glucopyranoside (I). This new saponin is named jurubine so as to correspond to the vernacular designation "Jurubeba" of the investigated plant which is indigenous to tropical Brazil (cf. 4). As already reported (5), acid hydrolysis of the glucoside jurubine afforded the sugar-free steroid jurubidine, $C_{27}H_{45}NO_2$, the structure of which was shown to be (25S)-3ß-amino-5α.22αO-spirostane (VII). The same aminospirostane VII has also been obtained by enzymic cleavage of I using emulsin. This demonstrates that spontaneous and stereo-


Ac2O - Pyridine
I : R = NH2 (Jurubine)
II : R = N=CH-
III : R = N=CH-Br
I
H+ or Emulsin
V
or
VI
AcOH
IV
IX
H2 - PtO2
VII : R = NH2 (Jurubidine)
VIII : R = NHAc
Ac2O - Pyridine HCl
X
H+
1. H2 - PtO2
2. OH-
XIII
XI : R = CH2-OH , XII : R = COOH

specific cyclization of the primary aglycone 3ß-amino-5α-furostane-22α.26-diol (V) or of the corresponding Δ^{22}-unsaturated dehydration product VI occurs easily under these very mild conditions (cf. 6).

Jurubine (I) ($C_{33}H_{57}NO_8$, amorphous, $[\alpha]_D$ -27.8° in pyridine) was characterized as its N-salicylidene derivative II ($C_{40}H_{61}NO_9$, m.p. 176-177°, $[\alpha]_D$ -34.9° in pyridine, -46.2° in $CHCl_3$), its N-4-bromo-benzylidene derivative III ($C_{40}H_{60}BrNO_8$, m.p. 195-200°, $[\alpha]_D$ -34.5° in pyridine) and its pentaacetyl derivative IV ($C_{43}H_{67}NO_{13}$, m.p. 165-168°, $[\alpha]_D$ -41.1° in pyridine). The i.r. spectrum of IV between 850 and 1000 cm^{-1} is quite similar to that reported by Wall et al. (2a) for sarsasaponin acetate. This is in accord with the observations of Hirschmann and Hirschmann (6) that spirostanes and the corresponding ring F-opened hemiketals of type V exhibit i.r. absorption maxima between 890 and about 1200 cm^{-1} at almost identical wave numbers although there are some differences in the intensities of absorption.

The structure I of jurubine has been proven in the following way: Acid or enzymic hydrolysis of I afforded, in addition to VII, one mole of D-glucose which was identified by paper and thin-layer chromatography. Pentaacetyl-jurubine (IV), obtained by acetylation of I with acetic anhydride-pyridine, gave, on dehydration with boiling acetic acid, the furost-20(22)-ene derivative IX (i.r. maximum at 1697 cm^{-1}, enol ether). Hydrogenation of IX

with platinum in acetic acid yielded the dihydro compound X which, after hydrolysis, gave (25S)-3ß-acetylamino-5α.20αH.22αH-furostan-26-ol (XI) ($C_{29}H_{49}NO_3$, m.p. 235-236°, $[\alpha]_D$ -19.6° in $CHCl_3$). This compound has been found to be identical in every respect with XI obtained from N-acetyljurubidine (VIII) (5) by isomerization with acetic anhydride-pyridine hydrochloride, yielding pseudo-jurubidine N.O-diacetate (XIII), followed by platinum catalysed hydrogenation of XIII and subsequent partial hydrolysis of the reduction product. XI has been oxidized with Kiliani reagent giving (25S)-3ß-acetylamino-5α.20αH-22αH-furostan-26-oic acid (XII) ($C_{29}H_{47}NO_4$, m.p. 246-248°, $[\alpha]_D$ -12.9° in $CHCl_3$) and so confirming that the glucose in jurubine (I) is attached to the primary hydroxyl at C-26 of the steroidal aglycone. The ß-D-pyranoside structure of the glucose portion in I is deduced from its facile cleavage by the ß-glucosidase emulsin (cf. 7). The configuration at C-22 is concluded to be 22R (α position of the hydroxyl) from the considerations advanced by Hirschmann and Hirschmann (6).

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