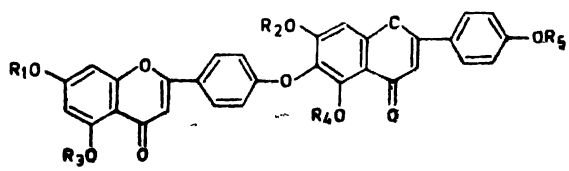
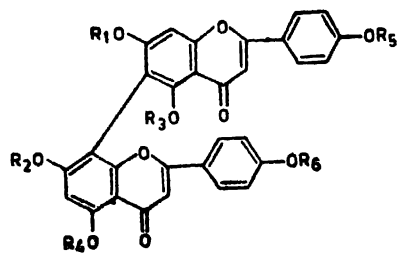
as JVIMI, JVIMII, JVIMIII and JVIMIV. They were separated by plc and characterized as hexa-O-methyl amentoflavone, hexa-O-methyl cupressuflavone, hexa-O-methyl robustaflavone and hexa-O-methyl agathis flavone (**Ib**), respectively by comparison of their nmr data with those of authentic samples.



II : $R_1=R_2=R_3=R_4=R_5=H$
IIa : $R_1=R_3=R_4=R_5=H$; $R_2=OH_3$



Ia : R=H ; Ib : $R=OH_3$

The compound (**Ib**), mol. wt. 622 (mass) melted at 162-164°. NMR data of (**Ib**) taken in $CDCl_3$ are δ : 2.12 (d, J=9 Hz, H-I-2', I-6') ; 2.99 (d, J=9 Hz, 2H, H-I-3', I-5'); 2.63 (d, J=9 Hz, s, 2H, H-II-2', II-6') ; 3.22 (d. J=9 Hz s, 2H, -II-3', II-5') ; 3.09 (s, 1H, H-I-8) ; 3.36 (s, 1H, H-II-6) ; 3.47, 3.49 (s, 1H, H-I-3, H-II-3) ; 6.26 (s, 3H, OCH_3-I-4') ; 6.22 (s, 3H OCH_3-II-4) ; 6.41 (s, 3H, OCH_3-I-7) ; 6.12 (s, 3H, OCH_3-II-7) ; 6.41 (s, 3H, OCH_3-I-5) ; 5.95 (s, 3H, OCH_3-II-5).

The compound **JVII**, m.p. 345°, gave pentaacetate, m.p. 240° and methylether, m.p. 268-70°. It was characterized as hinokiflavone (**II**) by nmr studies.

JVIII, m.p. 315°, gave a tetraacetate, m.p. 196-98° and a methylether, m.p. 268-70°. The structure was finally established as isocryptomerin (**IIa**) by comparison of the physical data and nmr studies of its acetate with those of authentic sample.

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C_{28}-Steroidal Lactones of the Seeds of *Nicandra physaloides*

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NICANDRA physaloides Gaertn, which is a herb and grows wildly in the hilly regions of India during the rainy season, belongs to the family Solanaceae[1]. The plant is well known for its insect repellant property and the aqueous extract of the leaves, from which 17 steroidal compounds have been isolated, has been shown to inhibit feeding of larvae of various insect species[2].

In continuation of our search for C_{28}-steroidal lactones from the solanaceous plants[3] and in view of the absence of any phytochemical report on the seeds of *N. physaloides*, this part of the plant material was taken up for chemical investigation. Chromatographic resolution of the ether soluble fraction of the alcoholic extract of defatted seeds (1.5 kg) of *N. physaloides* resulted in the isolation of four steroidal constituents from C_6H_6-EtOAc (3 : 1) eluates. The major compound was characterised as withanicandrin[4] (**I**) from detailed spectral analysis and also by direct comparison with an authentic sample. Out of the three minor compounds one, named as nicandrine B, was proved to be a new withanolide and its structure determination has been communicated elsewhere[5]. The present communication describes the characterisation of the third compound, provisionally designated as **NS-3**.

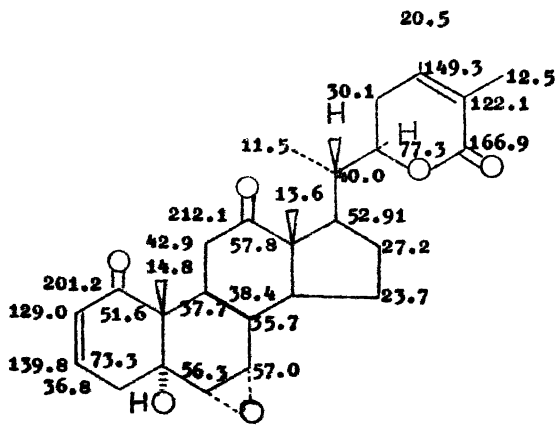
NS-3, $C_{28}H_{36}O_7$ (M^+ at m/z 484), m.p. 296-98°, $[\alpha]_D^{25}$ +53.3° ($CHCl_3$, *c* 0.13) showed striking resemblance with its congener, withanicandrin ($C_{28}H_{36}O_6$) in its spectral properties. Further, most of the parameters of ^1H nmr signals of **NS-3** were very similar to those of the corresponding hydrogen signals of withanicandrin pointing to structural similarity of these two compounds. While the carbonyl absorbtion band at 1680 cm^{-1} in the ir spectrum indicated the presence of an enone grouping, its presence in **NS-3** as a steroidal Δ^2-1-one system became amply manifest from its ^1H nmr spectrum which showed two olefinic hydrogen signals at δ 5.86 (1 H, *dd*, J=10, 2.5 Hz) and 6.60 (1 H, *ddd*, J=10, 5, 2.5 Hz).

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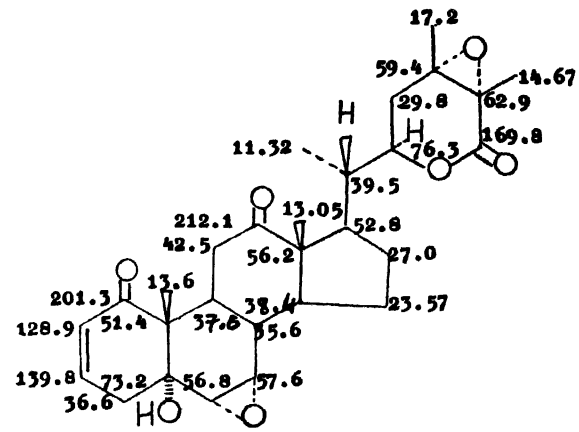
A 6α,7α-epoxy system in NS-3 was ascertained from the two mutually coupled carbinyl hydrogen signals at δ 3.08 (1 H, *d*, J=4 Hz) and 3.41 (1 H, *d*, with fine splitting) which corresponded to the 6- and 7-hydrogens of 5α-hydroxy, 6α,7α-epoxy steroid, like withanicandrin. The negative Cotton effect at 335 nm ($\Delta\epsilon - 1.70$) in the CD spectrum also indicated 5α configuration[6] of NS-3. The presence of 12-oxo function in NS-3 became apparent from the correspondence of ^{1}H nmr signals for 18, 19 and 21-methyl groups (δ 1.09 3 H, *s*, 1.24, 3 H, *s* and 0.89 3 H, *d*, J=6 Hz) with those of withanicandrin. In fact, a comparison of ^{13}C nmr spectrum of NS-3 with that of withanicandrin showed that the resonance originating from carbon atoms of the A, B, C and D rings of the compounds were in perfect agreement. So it was logically assumed that the two molecules differed only in the side chain.

Though the diognostic C-22-H of the δ-lactone was discernible at δ 4.56 (1 H, *dt*, J=11.2, 3 Hz) in the ^{1}H nmr spectrum of NS-3, the ir spectral band at 1730 cm^{-1} indicated an epoxy δ-lactone[7] rather than an α,β-unsaturated δ-lactone. The appearance of 27- and 28-methyls at δ 1.50 and 1.57 is also consistent with an epoxylactone structure as the chemical shifts of these two methyls are higher than those observed for vinylic methyls. In the CD spectrum the positive Cotton effect at 285 nm ($\Delta\epsilon$ +0.90) demonstrated the absolute configuration of C-22 to be R[8]. The mass spectrum of NS-3 showed in addition to an intense peak at m/z 125 (*a*), a small peak at m/z 141 (*b*) the genesis of which can also be explained on the basis of an epoxylactone structure.

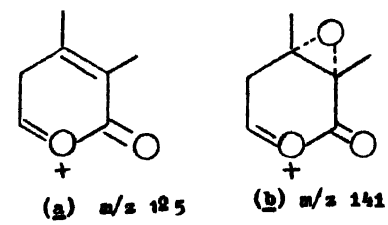
Based on these observations and from ^{13}C nmr data, NS-3 was proved to have the structure (II) which represents daturalactone-2[7] (daturalactone A)[9], isolated from the leaves of *Datura quercifolia*. The identity of NS-3 with daturalactone-2 was finally settled by direct comparison (^{1}H nmr) of the two samples. The CMR data of withanicandrin (I) and daturalactone-2 (II) are summarized around the expressions (I) and (II).



I



II



(a) m/z 125 (b) m/z 141

This is the first report of isolation of daturalactone-2 from a *Nicandra* species.

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