FUROCOUMARINS FROM THE FRUIT OF *AMMI VISNAGA*

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Chemical examination of the fruits of *Ammi visnaga* L. collected in Pakistan has led to the isolation of two furocoumarins, namely, 9-methoxy-7H-furo(3,2-g) (1) benzopyran-7-one (xanthotoxin) and 9-[(3-methyl-2-butenyl)oxy]-7H-furo-(3,2-g) (1) benzopyran-7-one (ammidin). These compounds have not been previously isolated from *A. visnaga*. Their uv, ir, ^{1}H- and ^{13}C-nmr spectra agreed with the reported data (1-3).

EXPERIMENTAL

PLAND MATERIAL.—The whole plants of *A. visnaga* were collected near Peshawar, Pakistan, and identified by Mr. Shahid Farooq, taxonomist, PCSIR Laboratories, Peshawar. A voucher specimen is deposited in the Herbarium of PCSIR Laboratories.

EXTRACTION AND ISOLATION.—The dried, powdered fruits of *A. visnaga* (800 g) were extracted (Soxhlet) with petroleum ether (60-80°). The extract was concentrated, filtered, and dissolved in MeOH. After decolorization with charcoal, the MeOH was removed and the residue crystallized from hexane to give xanthotoxin (0.2 g), mp 101-102°.

The remaining plant material was then extracted with EtOH. The solvent was removed and the residue dissolved in 10% HCl. The solution was basified with NH_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was decolorized, dried, and solvent was removed in vacuo. The crude product was crystallized from MeOH to give ammidin (0.105 g), mp 129-130°.

The coumarins were identified by standard spectral data as well as by comparison with corresponding published data (2;3).

Full details of the isolation and identification of the compounds are available on request to either senior author.

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3-*O*-ACETYLCYCLOART-23-EN-25-OL FROM THE ROOTS OF *SAPIUM INSIGNE*

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Sapium insigne Trimen has been used in Indian folk medicine for various ailments (1), but no chemical investigation has been made so far on its roots. We have isolated and characterized 3-*O*-acetylcycloart-23-en-25-ol from this plant.

The isolated compound gave all the positive tests for a triterpenoid. It was unchanged on treatment with Ac_2O/C_5H_5N at room temperature (24 h), but acetylation (Ac_2O/C_5H_5N) at reflux temperature (6 h)

yielded a substance whose ir spectrum lacked the band for a hydroxyl group and whose ^{1}H-nmr spectrum exhibited resonances for two acetate groups (δ, 2.01, s, 3H and 2.10, s, 3H). This experiment indicates the presence of a tertiary hydroxyl group in the original compound. Deacetylation of the compound with 2N NaOH (1 h) afforded cycloart-23-en-3β,25-diol as confirmed by comparison (mmp and co-tlc) with an authentic sample [isolated from *Tricholepis glaberrima* (2)]. These results indicate that the compound is 3-*O*-acetylcycloart-23-en-25-ol. This structure was further confirmed by conversion of the compound into known derivatives. Thus, catalytic hydrogenation afforded cycloartanol acetate (3) (mmp and co-tlc) and 25-hydroxycycloartanol acetate (2) (mmp and co-tlc). The latter product on deacetylation (2N NaOH) yielded 25-hydroxycycloartanol (4) (mmp and co-tlc). Hydroxylation of the original compound (OsO_4/Et_2O) afforded 3β-acetoxycycloartane-23, 24, 25-triol, mp, 183-187° (lit. mp 184-188°) (4). Hence, the original compound can be formulated as 3-*O*-acetylcycloart-23-en-25-ol which is reported for the first time in nature, although it has previously been prepared by mild acetylation of cycloart-23-en-25-ol (4).

EXPERIMENTAL

PLANT MATERIAL.—Plant material was procured from the United Chemicals and Allied Product, Calcutta, India, and authenticated by Botanical Survey of India, Allahabad Circle, U.P., India.

EXTRACTION AND ISOLATION.—The air-dried and powdered roots (3 kg) of *S. insigne* were extracted with rectified spirit (95% EtOH). The alcoholic extract (30 liters) was concentrated (1 liter) under reduced pressure and kept in a refrigerator for 10 days. It deposited a dirty colored amorphous substance which was filtered. The above substance was passed through a column of alumina, eluted with *n*-BuOH and crystallized with $CHCl_3$-Et_2O mixture as white microcrystalline solid (yield 2.00 g). The homogeneity was checked by tlc plates (Si-gel), Rf 0.56 ($CHCl_3$-MeOH, 2:8) and 0.25 ($CHCl_3$-C_6H_6, 3:7) respectively showing the presence of a single entity. (Found; C, 79.30; H, 10.69; $C_{32}H_{52}O_3$ required; C, 79.33; H, 10.74%). The ir spectrum of the compound (KBr, cm^{-1}) showed the absorptions 3400 and 1120 (OH), 2950 and 2870 (Me), 1725 (OAc), 1375 and 1365 (gem Me_2), 1010 (cyclopropane bridge), 1395, 1250, 1210, and 780 (-CH=CH-) and its ^{1}H-nmr spectrum displayed signals at δ 0.33 and 0.58 (a paired d, J=3.0 Hz, 2H, cyclopropane ring), 0.79 (s, 3H, 1×CH_3), 0.87 (s, 3H, 1×CH_3), 0.93 (s, 3H, 1×CH_3), 0.95 (d, J=6.0 Hz, 1×>CH-CH_3), 1.00 (s, 3H, 1×CH_3), 1.30 (s, 6H, substituted propane-2-ol), 1.31-2.00 (complex pattern, polymethylene-CH_2 and -CH protons), 2.02 (s, 3H, 1×OAc), 4.50 (t, J=4.0 Hz, 3α-H in secondary acetate group) and 5.60 (m, vinylic-H). The mass spectrum of the compound exhibited fragments at *m/z* 484 (M^+), 469 (M^+-CH_3), 466 (M^+-H_2O), 451 (M^+-CH_3-H_2O), 425 (M^+-$OCOCH_3$), 397 (M^+-C_5H_9O-2H), 381 (M^+-$OCOCH_3$-H-C_3H_7), 325 (M^+-$OCOCH_3$-H-$C_6H_{11}O$), 297 (M^+-$OCOCH_3$-H-$C_8H_{15}O$), 223 (M^+-$C_{17}H_{25}O_2$), and 182 (M^+-$C_{21}H_{34}O$), respectively.

ACETYLATION OF THE COMPOUND AT REFLUX TEMPERATURE.—The compound (100 mg) was acetylated with Ac_2O (6 ml) and C_5H_5N (6 ml) as usual under reflux condition for 6 h. The product was crystallized from Et_2O, mp 105-108°, λ max (MeOH) 205 nm. Found; C, 77.28; H, 10.00; $C_{34}H_{54}O_4$ required; C, 77.56; H, 10.26%; ^{1}H nmr ($CDCl_3$, Me_4Si, 60 MHz, δ) 0.33, 0.58, 0.79, 0.86, 0.92, 0.95, 1.00, 1.30, 1.31-2.00, 2.01, 2.10, 4.50, and 5.60.

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