para-Hemigossypolone: a Sequiterpenoid Aldehyde Quinone from *Gossypium hirsutum*

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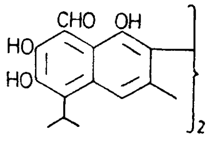
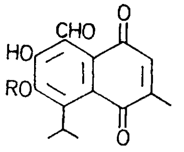
Summary A sesquiterpene aldehyde, *para*-hemigossypolone (8-formyl-6,7-dihydroxy-5-isopropyl-3-methyl-1,4-naphthaquinone), which inhibits the growth of *Heliothis virescens* (tobacco budworm), was identified as a constituent of flower buds (squares) from bollworm-resistant cotton (*Gossypium*).

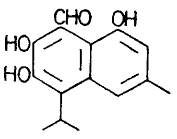
Gossypol (**1**), a triterpenoid aldehyde found in cotton, inhibits growth of *Heliothis virescens* (tobacco budworm) and *Heliothis zea* (bollworms) when addded to artificial or natural insect diets.[1] A recent survey (unpublished) of the U.S.A. wild cotton germ plasm collection has indicated the presence of several terpenoid aldehydes other than gossypol in cotton flower buds (squares). The amounts of these aldehydes present in the cotton buds correlated closely with *Heliothis* resistance in 120 accessions of cotton. Diethyl ether extracts of lyophilized cotton square powders from the different strains of cotton were analysed by n.m.r. spectroscopy. *Heliothis*-resistant strains gave extracts with spectra showing up to 5 signals between δ 12 and 9 (typical for aldehydic protons), while extracts from susceptible lines produced spectra with a single prominent signal at δ 11·0 for the aldehyde protons of gossypol.



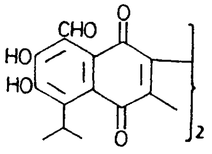
(1)



(2) R = H
(3) R = Me



(4)



(5)

One of these compounds, (**2**), m.p. 166·5—169 °C[2] ($CHCl_3$), was purified by t.l.c. It strongly inhibited the growth of *H. virescens*. Structure (**2**) was assigned to this compound on the basis of its ^1H and ^{13}C n.m.r. and mass spectra and from its synthesis from hemigossypol (**4**).[3]

High resolution mass spectrometry of (**2**) confirmed the molecular formula $C_{15}H_{14}O_5$. Prominent peaks appeared at *m/e* 274(83%, M^+), 259 (100%, $M^+ - Me$), 231 (21%, $M^+ - Me - CO$) and 203 (5%, $M^+ - Me - 2\,CO$). These fragmentations are in agreement with a quinonoid-type structure.[4]

The ^{13}C n.m.r. spectra confirmed that (**2**) was a 1,4-naphthoquinone. Its quinone carbonyl peaks appeared at δ 187·6 and 186·5 p.p.m. In gossypolone (**5**)[3] these carbonyl groups appeared at δ 186·5 and 183·5 p.p.m. 1,2-Naphthaquinone carbonyl groups resonate at δ *ca.* 180.[5]

The ^1H n.m.r. spectrum ($CDCl_3$) of (**2**) exhibited signals at δ 10·70 (aldehyde), 6·50 and 12·95 (OH, established by D_2O exchange), 1·42 (6H, d, Me, *J* 6·9 Hz), and 2·14 (3H, d, Me, *J* 1·6 Hz). Spin decoupling indicated that the protons at δ 1·42 were coupled to a septet at δ 4·13 (1H), and the Me group at δ 2·14 was coupled to an aromatic proton at δ 6·62 (1H).

Seshadri[2] reported the isolation of 6-methoxyhemigossypolone (**3**) from *Bombax malabaricum* DC root bark and also tentatively identified (**2**), m.p. 167—168 °C, from this source. Spectral data were not reported. We proposed the name *para*-hemigossypolone for (**2**) based on the terminology devised for gossypolone.[3]

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