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NONALKALOIDAL CONSTITUENTS OF BUXUS PAPILOSA

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Two new steroidal alcohols provisionally named and formulated as buxpapinol, $C_{27}H_{46}O$, m.p. 183–184°C, and buxpapininol, $C_{22}H_{36}O_2$, m.p. 248–251°C, have been isolated from the alcoholic extracts of *Buxus papilosa*.

Buxus papilosa which grows gregariously on limestone,[1] has already been found[2] to contain a number of steroidal alkaloids. This paper describes the isolation and some of the properties of two new steroidal alcohols, provisionally named as buxpapinol and buxpapininol.

Buxpapinol, $C_{27}H_{46}O$, m.p. 183–84°C, gave positive tests for sterols. Its IR spectrum showed bands at 3390 (-OH), 1639 cm^{-1} (probably —C=C—), and 1075 cm^{-1} (probably secondary OH). The NMR spectrum showed complex peaks centred at 9.4 (probably cyclopropane protons),[3] 9.22, 9.16 (probably a secondary methyl group), 9.04 (probably a tertiary methyl group), 8.7 (very strong peak, accounting for 6 protons), 8.54, 8.29 (probably methylenes of the steroidal nucleus), and 5.22 τ (one proton, probably, —C*H*—CH_3). Buxpapinol acetate showed IR bands at 1739 (C=O), 1647 (C=C) and 1250 cm^{-1} (CO, ester); the nuclear magnetic resonance spectrum of the acetate showed identical peaks to those of free alcohol except for an additional peak at 7.94 τ (CH_3CO).

Buxpapininol, $C_{22}H_{36}O_2$, m.p. 248–251°C also gave positive tests for sterols. The IR spectrum showed bands at 3450 (—OH), 1625 cm^{-1} (C=C). The NMR spectrum showed peaks at 9.22, 9.15, 9.03 (accounting for 9 protons, probably a secondary and two tertiary methyl groups), 8.74, 8.60, 8.31 (complex peaks, probably methylenes of steroidal nucleus) and 5.23 (one proton, probably CH—CH_3). Buxpapininol acetate showed IR bands at 1739 (very strong, C=O of ester), 1704 (shoulder), 1645 (—C=C—), 1250 cm^{-1} (very strong; C=O of ester), and NMR peaks at 9.15 (singlet, probably two tertiary methyl groups), 8.98 (doublet, J=3.6 c/s, probably a secondary methyl group), complex peaks between 8.72–8.31 (probably methylenes of the steroidal nucleus), 7.93 (singlet, probably, CH_3—CO), and 5.31 (one proton multiplet, probably CH—CH_3).

Work is in progress to study the structure of these new steroidal alcohols.

Experimental

The shade-dried whole plant of *Buxus papilosa* (dry weight, 4 kg) was cut into small pieces and extracted with 95% ethyl alcohol (8 gallons) at room temperature. The alcoholic extract was concentrated under reduced pressure to a thick syrup. The syrupy residue was acidified with 5% acetic acid, kept in a refrigerator for 2 days and filtered. The acidic filtrate was saved for the alkaloids and the residue was worked up for its nonalkaloidal constituents.

The residue was treated with excess chloroform and the mixture was warmed and filtered. The chloroform-insoluble portion was dissolved in petroleum ether, charcoaled again and again, dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure to give a brownish mass.

Isolation of Buxpapinol.—The brownish mass was refluxed with 10% alcoholic potassium hydroxide for 4 hr and the reddish brown solution was allowed to cool. Sufficient distilled water was added until a white curdy precipitate was obtained. This was extracted with chloroform, chloroform extract was charcoaled, dried over anhydrous sodium sulphate and solvent removed under reduced pressure to give a thick syrup which crystallized from methanol to give white crystals, m.p. 183–184°C. Repeated recrystallization did not raise its melting point. (Found: C, 84.08; H, 11.77; O, 4.16%; $C_{27}H_{46}O$ requires: C, 84.0; H, 11.86; O, 4.14%.)

The IR spectrum (Nujol) showed bands at 3390, 3012, 2941, 1639, 1460, 1372, 1075, and 1075, and 1030 cm^{-1}. The NMR spectrum ($CDCl_3$) showed peaks at 9.4, 9.22, 9.16, 9.04, 8.7, 8.29 and 5.22 τ.

Acetylation of Buxpapinol.—Buxpapinol (1 g) was added to a solution of acetic anhydride (10 ml) and dry pyrine (10 ml). The mixture was refluxed for 4 hr cooled and poured on to crushed

ice and left overnight. The crude acetate obtained on filtration was recrystallised from methanol to give white needles, m.p. 140–141°C.

The IR spectrum (Nujol) showed bands at 3012, 2941, 1739, 1647 and 1250 cm^{-1}. The NMR spectrum ($CDCl_3$) showed peaks at 9.47, 9.15, 9.06, 8.76, 8.72, 8.57, 8.37, 7.94 and 5.12 τ.

Isolation of Buxpapininol.—The chloroform-soluble portion was charcoaled again and again and dried over anhydrous sodium sulphate. The filtered solution was concentrated under reduced pressure to a thick syrup which gave a white crystalline compound, m.p. 248–251°C. (Found: C, 79.84; H, 10.65; O, 9.22%. $C_{22}H_{36}O_2$ requires: C, 79.82; H, 10.84; O, 9.63%.)

The IR spectrum (Nujol) showed bands at 3450, 1665, 1625, 1460, 1370 and 1075 cm^{-1}. The NMR spectrum ($CDCl_3$) showed peaks at 9.22, 9.15, 9.03, 8.74, 8.60, 8.31 and 5.23 τ.

Acetylation of Buxpapininol.—Buxpapininol was acetylated by the same general procedure as described above to give white needles, m.p. 183–184°C. The IR spectrum (Nujol) showed bands at 1739, 1704, (shoulder) 1645 and 1250 cm^{-1}. The NMR spectrum ($CDCl_3$) showed peaks at 9.15, 9.01, 8.95, 8.72, 8.59, 8.31, 7.93 and 5.31 τ.

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