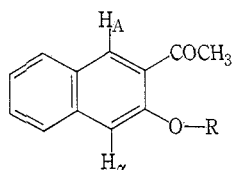
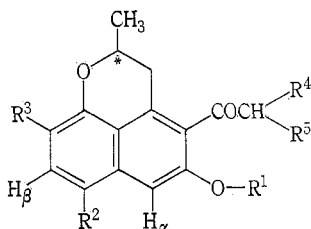


STUDIES ON XANTHORRHOEA RESINS*

V.† BROMO DERIVATIVES OF XANTHORRHOEOL

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In the course of work on the constitution of xanthorrhoeol (I)¹ an unsuccessful attempt to degrade the acetyl side-chain of xanthorrhoeol methyl ether (II)¹ by the action of hypobromite led to a crystalline dibromo derivative (III). Substitution had occurred in the nucleus (n.m.r.). A similar attempt with the acetyl derivative of xanthorrhoeol (IV)¹ gave a mixture of products only one of which, a tetrabromo derivative (V), was isolated. For several reasons it appeared interesting to study the bromination of xanthorrhoeol methyl ether, and by the choice of appropriate



(VIII) R = Ac

(IX) R = H

	R ¹	R ²	R ³	R ⁴	R ⁵
(I)	H	H	H	H	H
(II)	Me	H	H	H	H
(III)	Me	Br	Br	H	H
(IV)	Ac	H	H	H	H
(V)	Ac	Br	Br	Br	Br
(VI)	Me	Br	Br	Br	H
(VII)	Me	Br	Br	Br	Br

conditions di-, tri- (VI), and tetra-bromo derivatives (VII) were obtained. Higher bromination was not possible. The third and fourth bromine atoms entered the acetyl side-chain. These structural assignments are fully supported by n.m.r. measurements (Table 1) and the chemical shifts for the brominated side-chain fall close to the values predicted by the application of Shoolery's rules.² The aromatic proton region contains only two protons, H_α and H_β, which appear as singlets. Their chemical shifts are easily established, for the acetyl derivative shows the typical

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¹ Duewell, H., *Aust. J. Chem.*, 1965, **18**, 575.

² Dailey, B. P., and Shoolery, J. N., *J. Am. chem. Soc.*, 1955, **77**, 3977.

downfield shift of the resonance line of the "ortho" proton (H_α) due to deshielding by the acetyl carbonyl group. This downfield shift is also shown in the n.m.r. spectra of the acetyl derivatives of xanthorrhoeol (IV) and of its simple analogue 3-acetoxy-2-acetylnaphthalene (VIII)³ when compared with their parent compounds, viz. xanthorrhoeol and 2-acetyl-3-hydroxynaphthalene (IX)⁴ respectively. In the simpler naphthalene this shift, due to the changed steric situation, is, however, only 0.25 p.p.m. as against about 0.5 p.p.m. in the xanthorrhoeol derivatives.

TABLE 1
SUMMARY OF CHEMICAL SHIFT VALUES (τ)

	OCH ₃	OCOCH ₃	COCH ₃	COCH ₂ Br	COCHBr ₂	H _{α}	H _{β}	H _A
(I)	—	—	7.37	—	—	2.94	—	—
(II)	6.12	—	7.49	—	—	3.02	—	—
(III)	6.01	—	7.47	—	—	2.68	2.17	—
(IV)	—	7.72	7.51	—	—	2.54	—	—
(V)	—	7.62	—	—	3.50 ^b	2.11	2.08	—
(VI)	5.99	—	—	5.62 ^a	—	2.66	2.13	—
(VII)	5.97	—	—	—	3.28 ^b	2.68	2.15	—
(VIII)	—	7.67	7.43	—	—	2.55	—	1.78
(IX)	—	—	7.34	—	—	2.80	—	1.80

^a Value from Shoolery's rules 5.74.

^b Value from Shoolery's rules 3.41.

Experimental

Melting points are uncorrected and were determined on a Kofler hot-stage. N.m.r. spectra of solutions in deuteriochloroform were measured with a Varian A60 spectrometer using tetramethylsilane as internal standard.

Dibromoxanthorrhoeol Methyl Ether (II)

Xanthorrhoeol methyl ether (200 mg, 7.8×10^{-4} mole) was dissolved in glacial acetic acid (7 ml) and a 5% bromine solution in glacial acetic acid (v/v, 1.7 ml, 15.6×10^{-4} mole) added at room temperature. The crystals formed were collected (214 mg, 66%) and washed successively with a little alcohol, saturated sodium hydrogen carbonate, and water. After one recrystallization, the material melted at 169–171°. Further purification by preparative t.l.c. on silica gel G (Merck) using benzene as the developing solvent (R_F about 0.6, bright yellow fluorescence in u.v. light) gave 4-acetyl-7,9-dibromo-5-methoxy-2-methyl-2H,3H-naphtho[1,8-bc]pyran; fine pale yellow needle clusters from ethanol, m.p. 175–176° (Found: C, 46.7; H, 3.7; Br, 38.0. $C_{16}H_{14}Br_2O_3$ requires C, 46.4; H, 3.4; Br, 38.6%).

Tribromoxanthorrhoeol Methyl Ether (V)

To a solution of xanthorrhoeol methyl ether (200 mg, 7.8×10^{-4} mole) in glacial acetic acid (5 ml) the above bromine reagent (2.6 ml, 23.4×10^{-4} mole) was added at 40° and the mixture left overnight. The crystals separated were treated as for the dibromo derivative and gave material (295 mg, 77%) melting at 179°. Purification by preparative t.l.c. (R_F about 0.75 on silica gel G/benzene, dull brown in u.v. light) gave 7,9-dibromo-4-bromoacetyl-5-methoxy-2-methyl-2H,3H-naphtho[1,8-bc]pyran as fine pale yellow needles from ethanol, m.p. 181–182° (Found: C, 39.2; H, 2.8; Br, 48.8. $C_{16}H_{13}Br_3O_3$ requires C, 39.0; H, 2.7; Br, 48.6%).

³ Fries, K., and Schimmelschmidt, K., *Ber. dt. chem. Ges.*, 1925, **58**, 2840.

⁴ Duewell, H., and Haig, T. J., *J. chem. Soc. (C)*, 1968, 169.

Tetrabromoxanthorrhoeol Methyl Ether (VI)

Treatment of xanthorrhoeol methyl ether (201 mg, 7.8×10^{-4} mole) in glacial acetic acid (5 ml) with bromine reagent (3.5 ml, 31.2×10^{-4} mole) caused the separation of fine yellow needles in spherical clusters (331 mg, 74%). Recrystallization did not change the melting point (165–166°). Preparative t.l.c. (R_F about 0.8 on a silica gel G/benzene, dull brown in u.v. light) gave 7,9-dibromo-4-dibromoacetyl-5-methoxy-2-methyl-2H,3H-naphtho[1,8-bc]pyran as bright yellow fine needles from ethanol, m.p. 168–169° (Found: C, 33.45; H, 2.45; Br, 55.8. $C_{16}H_{12}Br_4O_3$ requires C, 33.6; H, 2.1; Br, 55.9%).

Note on the Above Preparations

The remaining reaction products were always precipitated by the addition of water and consisted of mixtures of bromo derivatives. T.l.c. made complete separation possible in every case.

Bromination of the Acetate of Xanthorrhoeol

The acetate of xanthorrhoeol (280 mg, 10^{-3} mole) in glacial acetic acid (2 ml) was treated with bromine reagent (5 ml, 5×10^{-3} mole). The bromine colour did not disappear and no crystals formed when left to stand overnight. A little sodium sulphite was added to destroy the excess of bromine and the reaction product precipitated by the addition of water (570 mg, m.p. 60–65°). Recrystallization from ethanol gave fine yellow needles, m.p. 132–133°, (260 mg, 44%) of 5-acetoxy-7,9-dibromo-4-dibromoacetyl-2-methyl-2H,3H-naphtho[1,8-bc]pyran (VII) (Found: C, 34.1; H, 2.3; Br, 53.6. $C_{17}H_{12}Br_4O_4$ requires C, 34.0; H, 2.0; Br, 53.3%).

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