The Structure of Nephroarctin

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NEPHROARCTIN (I), $C_{20}H_{20}O_7$, a new lichen substance, was isolated by Nuno[1] from *Nephroma arcticum* (L.) Torss., as colourless prisms, m.p. 192—193°, $[\alpha]_D^{23} = 0°$ (*c* 1·0 in $CHCl_3$), positive *p*-phenylenediamine,[2] $FeCl_3$, and KOH reactions. Acetylation of (I) afforded the hexa-acetate (II), $C_{32}H_{36}O_{15}$, colourless crystals, m.p. 178—179°, while bromination gave monobromonephroarctin (III), $C_{10}H_{19}BrO_7$, colourless prisms, m.p. 186—187°. The n.m.r. spectrum of (I) showed δ (in $CDCl_3$) 2·11 (6H, s, 2Me), 2·28 (3H, s, Me), 2·73 (3H, s, Me), 3·80 (3H, s, OMe), 6·61 [1H, s, aromatic proton, not observed for (III)], 10·18 and 10·33 (each 1H, s, CHO), and 13·43 and 13·79 p.p.m. [each 1H, s, OH, removed by D_2O, not observed for (II)], ν_{max} (KBr) 1745 (ester C=O) and 1634 cm.$^{-1}$ (aldehyde C=O), *m/e* 372 (M^+), 207 (RCO^+, S-fragment†), 166 (RO^+H, A-fragment†). The S-fragment corresponded to $C_{10}H_7O_5$ (calc. 207·02934. Found: 207·0311) and the A-portion fragment to $C_{10}H_{14}O_2$ (calc.: 166·09937. Found: 166·1012). The n.m.r. spectrum of the bromo-compound (III) showed *m/e* 207 (S-portion), 244 and 246 (A-portion), besides 450 and 452 (M^+). These data indicated that the most reasonable structure for (I) was the phenyl benzoate with 2 CHO, 2 OH, and Me on the S-ring and 3 Me, OMe, and H on the A-ring.

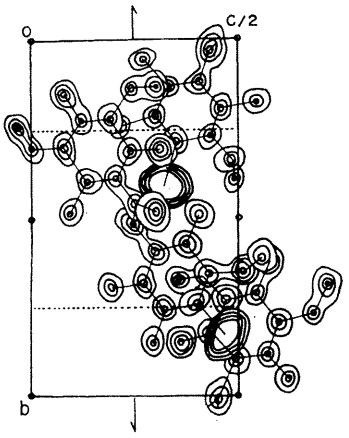
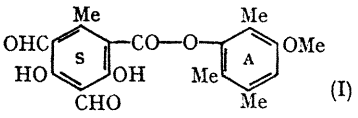


FIGURE. *The final electron-density distribution of* (III) *projected on* (100)

The relative positions of the substituents of (I) were determined from the *X*-ray crystal analysis of (III): space group $P2_1/c$ with $a = 15·25$, $b = 14·73$, $c = 18·18$ Å and $\beta = 104° 15'$. By the application of minimum function, least-squares, and Fourier syntheses, (I) was finally established as 3-methoxy-2,5,6-trimethylphenyl 3,5-diformyl-2,4-dihydroxy-6-methylbenzoate.



(I)

Both benzene rings of nephroarctin are associated with an unusually large number of C_1 substituents.

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† The designation commonly used in depside chemistry is employed.

[1] M. Nuno, unpublished work.
[2] Y. Asahina, *Acta Phytochim.*, 1934, **8**, 47.
[3] For mass spectrometric studies of depsides see S. Huneck, C. Djerassi, D. Becher, M. Barber, M. von Ardenne, K. Steinfelder, and R. Tümmler, *Tetrahedron*, 1968, **24**, 2707.