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FLAVANONE QUINONES FROM CYPERUS SPECIES

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It has previously been reported[1] that many Cyperus species are rich sources of naturally occurring quinones. Three flavanone quinones have been isolated and the sources and some properties are shown in Table 1.

TABLE 1

Compound	Formula	Source	m.p.	$[\alpha]_D^{20}$ ($CHCl_3$)
Remerin (1)	$C_{17}H_{14}O_7$	Remirea maritima	190-200 (dec.)	-300
Breverin (2)	$C_{18}H_{16}O_7$	Cyperus brevibracteatus	186-187°	-366
Scaberin (3)	$C_{19}H_{18}O_7$	C.scaber	184° (dec.)	-343

Remerin (1) crystallised from butanone as bright yellow plates. Acetylation gave a monoacetate and reductive acetylation with zinc and acetic anhydride a leuco-triacetate, indicative of a free hydroxyl group and a quinone. Catalytic hydrogenation gave a colourless quinol (4) which was reconverted to (1) on aerial oxidation. The u.v. spectrum of (4) [λmax 340 (sh) and 288 nm (log ε 4.00, 4.30)] was suggestive of a flavanone.

The n.m.r. spectrum of (1) showed two m- coupled aromatic protons at τ 3.91 (1H,d; J=2Hz) and 3.96 (1H,d; J=2Hz) together with a hydrogen bonded phenol at τ -1.86 (1H,s, exchanged with D_2O). Other signals at τ 7.1 (2H, octet), 4.52 (1H, octet) and 3.05 (1H, doublet) represented an ABMX system with J_{AB}=17Hz, J_{AM}=12Hz, J_{BM}=4Hz and J_{MX}=1.5Hz. The remaining signals were τ 4.05 (1H,s) and methoxy-resonances at τ 6.16 (3H,s) and 6.19 (3H,s). In the n.m.r. spectrum of (4) the ABMX pattern of (1) was seen as a typical

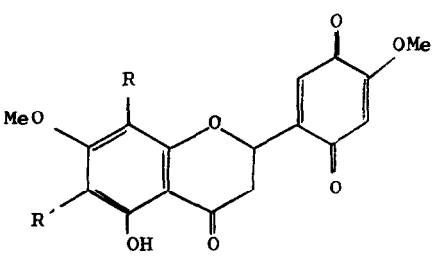
pattern of a flavanone. The new aromatic protons in the C ring appeared at τ 3.23 (1H,s) and 3.56 (1H,s) consistent with a 1,4 arrangement of these protons.

The mass spectrum of (1) gave further confirmation of its structure. The major fragment ions at 167 ($C_8H_7O_4$), 166 ($C_8H_6O_4$) and 164 ($C_9H_8O_3$) satisfy a retro Diels-Alder cleavage in the B ring.

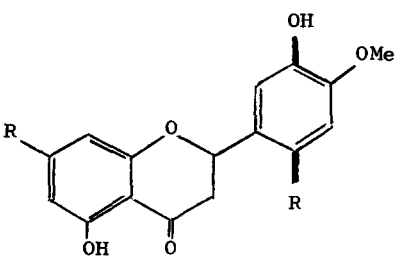
Confirmation of the structure of remerin came from its synthesis from (±)hesperetin (5). Methylation with dimethyl sulphate and potassium carbonate in acetone gave (6) which was oxidised to (1) in 50% yield by Fremy's salt.

The n.m.r. spectrum of scaberin (3) showed the replacement of the two m- coupled protons of (1) by a 6 proton methyl singlet at τ 7.92. The major fragment ions in the mass spectrum occurred at m/e 195, 194 and 164. Breverin was, similarly, shown to be represented by (2). Attempts to determine the position of the methyl group on the A ring of (2) by means of europium shifted n.m.r. failed due to ready ligand exchange between (2) and the ligand of the europium shift reagent.

To our knowledge, remerin and its homologues represent the first examples of unmodified flavanoid quinones found in nature.



(1) R=R′=H
(2) R or R′=Me R or R′=H
(3) R=R′=Me



(4) R=OMe R′=OH
(5) R=OH R′=H
(6) R=OMe R′=H

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References

1 R. D. Allan, R. W. Dunlop, M. J. Kendall, R. J. Wells and J. K. MacLeod Accompanying paper, and references therein.