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NOVEL DIMERIC CHALCONE-BASED PIGMENTS FROM *BRACKENRIDGEA ZANGUEBARICA*

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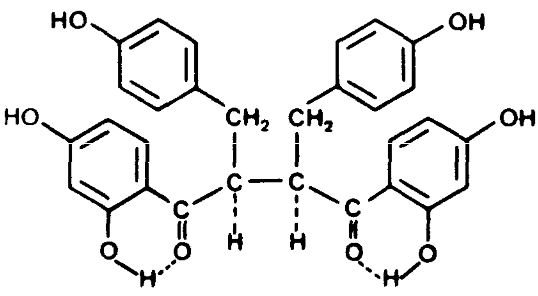
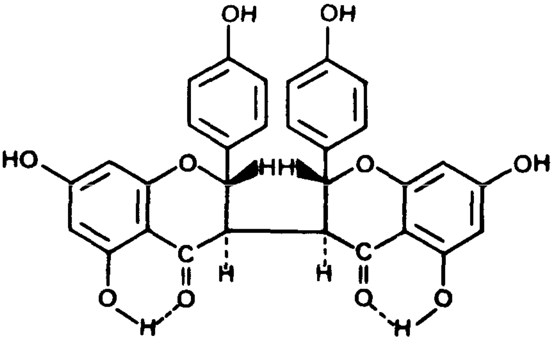
Summary: The structures of four dimeric yellow pigments from the bark of *Brackenridgea zanguebarica* have been established from the n.m.r. and mass spectral studies.

We have recently reported the isolation of a novel dimeric dihydrochalone named brackenin (1), from the bark of *Brackenridgea zanguebarica*[1], and we now report on further compounds from this source. The structures of these interrelated dimers are shown in (2),(3),(4) and (5).

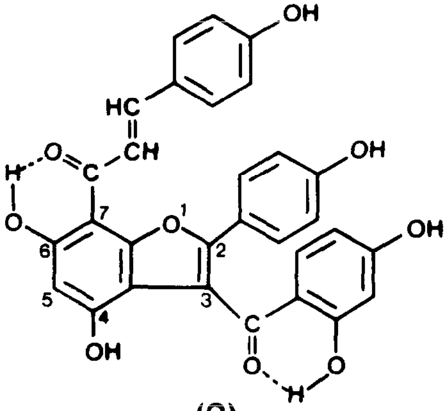
The intense yellow colour of the bark of the tree is largely due to (3), 4,6-dihydroxy-2-(4-hydroxyphenyl)-3-(2,4-dihydroxybenzoyl)-7-[3-(4-hydroxyphenyl) propenyl] benzofuran. The pigment (3) produces a deep red colour with ammonia (chalcone) and alkali fusion gave a high percentage of 4-hydroxybenzoic acid and some 2,4-dihydroxybenzoic acid. The orange needles, mp. 252-253 °C, had a molecular ion at 524 (f:524.108; c:524.111) and gave satisfactory elemental analysis for $C_{30}H_{20}O_9$. Further characteristic fragments were present at m/z 404 and 294. The 'H n.m.r. spectrum (at 300 MHz) showed two AA'BB' systems, an ABX system, a singlet and two typical chalcone protons (J=16.0 Hz). All four of the pigments had a downfield hydroxyl group (δ 14.0) typical of a phenolic OH hydrogen-bonded to C(4). The hexaacetate of (3), mp. 108-109 °C, its hexamethyl ether, mp. 109-111 °C, and the hydrogenated free phenolic form, mp. 250 °C (molecular mass increased by two mass units), provided further evidence for the proposed structure. Thus the hexamethyl ether had a strong molecular ion peak at 608 (f:608.204; c:608.202) corresponding to $C_{36}H_{32}O_9$. Characteristic fragments at m/z 165,161 and 135[2] and shown as (6), (7) and (8) respectively, confirmed the substitution pattern of the benzene rings.



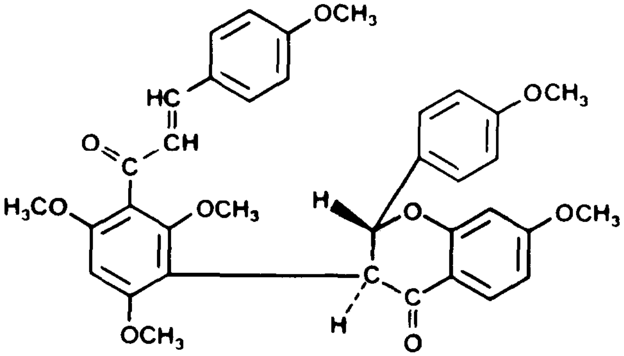
(1) BRACKENIN



(2) CHAMAEJASMIN

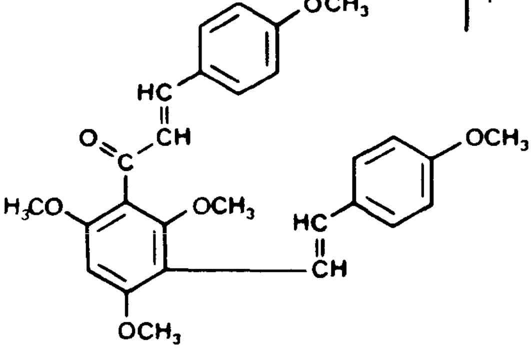


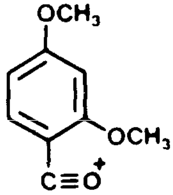
(3)



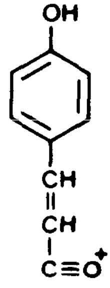
(5)

(4) TRANS–2,3–DIHYDRO–
DERIVATIVE OF (3)

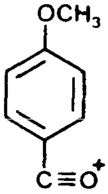




(6)



(7)



(8)

(9)

^{13}C n.m.r. spectra of the hexamethyl ether and hexaacetate of (3) established i) the presence of the carbonyl group of the α,β-unsaturated chalcone system, which shifted downfield (δ 190 → δ 202) on hydrogenation, and ii) the position and nature of attachment[3,4,5] of the 4-hydroxyphenyl, the 2,4-dihydroxybenzoyl and the 4-hydroxycinnamoyl moieties. The compound (4), mp. 66 °C, was found to be the dihydro derivative of (3) and its structure was readily deduced. The 'H n.m.r. spectrum (at 300 MHz) of its hexamethyl ether is similar to that of (3) with one important difference. The two protons of the dihydrofuran ring resonate as a sharp pair of doublets at δ 5.34 and δ 5.82 (J = 5.3 Hz). High resolution mass spectrometry on the molecular ion, $C_{36}H_{34}O_9$ gives 610.220 (c: 610.221).

Compound (2) mp. 86 °C, which was present only in trace amounts, was identified by analogy to brackenin (1). It has recently been isolated from *Thymeliacea spp.* by Chinese workers[6] and represents a rare type of biflavanone.

The last compound in the series (5), hexamethyl ether, mp. 69 °C, is isomeric with (4) but possesses a flavanone nucleus in place of the benzofuran. The chalcone portion of the molecule is unchanged from that present in (3) and (4). By contrast, the flavanone portion of the nucleus was not immediately obvious. The present assignment is supported by the presence of a set of doublets at δ 4.64 and δ 5.88 (J = 12.6 Hz), allocated to the *trans*-diaxial protons on C(2) and C(3) of the flavanone nucleus and other spectral evidence. The above set of doublets are broadened at 28 °C but sharpen up remarkably at 47 °C. This is indicative of restricted rotation about the bond connecting the two flavonoid moieties. The molecular ion for the hexamethyl ether at m/z 610 (f: 610.220; c: 610.221) corresponds to $C_{36}H_{34}O_9$. The base peak in the mass spectrum at m/z 460 (9) is readily rationalised as the product of a retro Diels-Alder fragmentation of the parent compound.

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