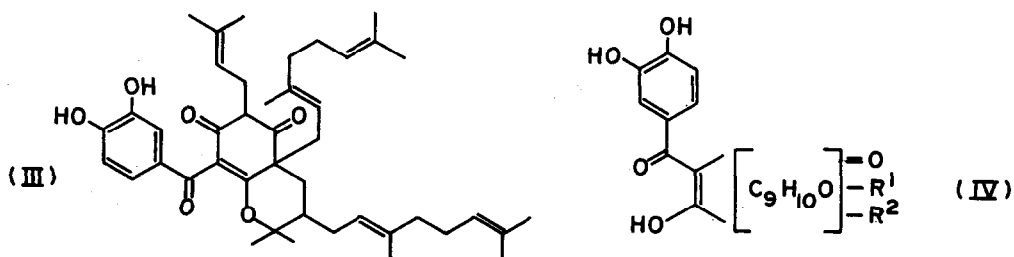
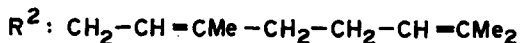
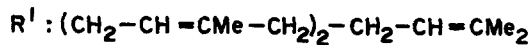
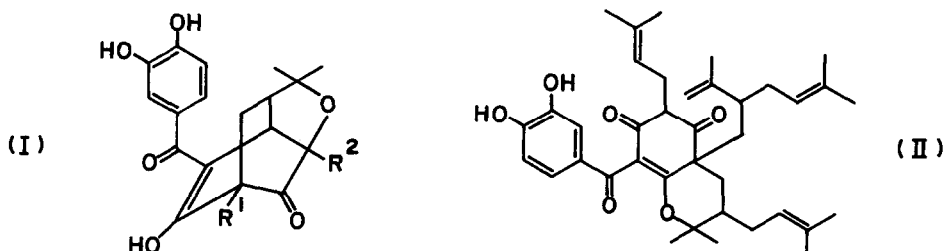


THE STRUCTURE OF BRONIANONE\*

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Ollis, Redman and Sutherland assigned structure (I) to bronianone,  $C_{43}H_{58}O_6$ , a deep yellow oil from the stem wood of Garcinia hombroniana.<sup>1</sup> In the light of the structure<sup>2</sup> of xanthochymol (II),  $C_{38}H_{50}O_6$ , and the very close resemblance between the two ketones in many of their properties, we conclude that bronianone has the structure (III), differing from (II) only in the nature of two of the side chains.



Ollis *et al.* have provided spectral and chemical evidence for the part structure (IV). The mass spectra of bronianone and its di- and trimethyl ethers showed the initial loss of  $C_{10}H_{17}^+$ , followed by the loss of  $C_{14}H_{24}$  in a single or 3-step process. The latter fragmentation is better explained by

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(III) than by (I); in (I)  $R^1$  will be lost as a  $C_{15}$  unit with subsequent further fragmentation, but in (III) the loss of  $C_5$ ,  $C_5$  and  $C_4$  units is to be expected.

The NMR spectra of bronianone and its methyl ethers show,<sup>1</sup> in addition to 3 aromatic H, 5 CH=, 8 allylic  $CH_2$ , 7 Me on C=, and 2 Me on saturated C (singlets at 8.92 and 9.23). The last two Me signals are at considerably higher field than the  $Me_2$  signals (8.52 or below) of the tetrahydrofuran ring in morellin and its analogues,<sup>3</sup> but they are much nearer to the Me signals (8.8; 8.95) of the chroman ring in xanthochymol. Structure (III), however, has one vinylic Me group more, and one methine and one allylic  $CH_2$  group less, than (I); it is doubtful if a clear choice between the two alternatives can be made on the basis of the 60 MHz spectrum of so complex a molecule.

One reason for Ollis *et al.* assigning the bicyclo [2.2.2] octenone type structure to bronianone is "an interesting biogenetic relation .... between the polyisoprenylated 'benzophenone' structure (I) and the polyisoprenylated xanthonoids" (the morellin group). In fact, a biogenetic approach to the structure of bronianone will lead almost inevitably to (III). The biosynthetic process<sup>2</sup> suggested for xanthochymol (II), starting from maclurin in which (unlike the biosynthesis of the morellin type) the target of prenylation is only the phloroglucinol half, is equally valid for bronianone (III). The only difference in the biosynthesis of (III) is that maclurin is progressively attacked by two prenyl and two geranyl units.

#### References

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2. Preceding paper
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