and the solvent removed. The crude crystalline product obtained, was recrystallized from Me_2CO–hexane to give **3** (200 mg), mp 190–196°. The analytical sample showed mp 208–212°, $[\alpha]_D$ +22.43 (2.23, MeOH), ν_{max} 3500, 1710 cm^{-1}, δ. 0.73 (*s*, C-10-Me), 1.17 (*s*, C-4-Me). (Found: C, 64.84; H, 8.16. $C_{16}H_{24}O_5$, requires: C, 64.33; H, 8.15%).

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CASTANOPSIN, A NEW TRITERPENE FROM *CASTANOPSIS INDICA**

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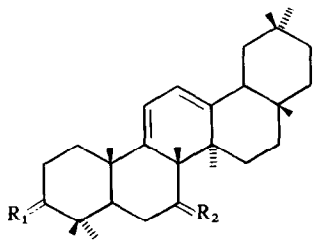
Key Word Index—*Castanopsis indica*; Fagaceae; castanopsin; pentacyclic triterpene; olean-9,12-diene-3β,7α-diol.

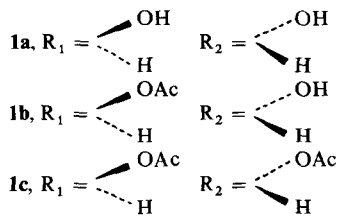
INTRODUCTION

In an earlier communication [1] structure elucidation of two triterpenoids, castanopsone and castanopsol, along with the isolation of castanopsin, another new triterpenoid from *Castanopsis indica* were reported. This paper describes the structure elucidation of castanopsin.

RESULTS

Castanopsin, mp 224–8°, $C_{30}H_{48}O_2$ (M^+ 440), showed the diagnostic colour reactions of unsaturated triterpenoids. The IR spectrum exhibited absorptions for OH (3575, 3290), *gem* dimethyl (1375, 1365) and a conjugated trisubstituted double bond (1630, 835 cm^{-1}). The NMR spectrum showed the signals for eight quaternary methyls in the region δ 0.83–1.2 ppm, two carbinolic protons at 3.78 (*q*) and 4.14 ppm (*t*, $W_{\frac{1}{2}}$ = 7 Hz) respectively and two protons on a *cis*-conjugated double bond as a pair of doublets at 5.53 and 5.71 (J = 6 Hz). The latter was supported by UV absorption (286 nm, log ε 3.9) due to the homoannular diene system in the molecule.





Acetylation of castanopsin at 0° gave a monoacetate (**1b**) mp 184–5°, whose IR spectrum still showed the presence of OH in the molecule. Its NMR spectrum exhibited an acetoxymethyl signal at δ 2.00 ppm and the corresponding geminal proton at 5.02 ppm. When acetylation was carried out at waterbath temperature, castanopsin yielded a diacetate (**1c**) whose IR spectrum was devoid of OH absorption and the NMR spectrum showed two acetoxymethyl signals at δ 2.00 and 2.03 ppm and two carbinolic protons at 4.93 and 5.36 ppm. Thus, the presence of two secondary OH groups in the molecule was confirmed and one of these was slightly hindered in nature.

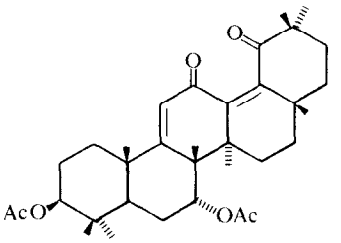
One OH group (3.78 ppm) was allocated to the C-3 position on biogenetic grounds. The SeO_2 oxidation of castanopsin diacetate yielded a dienedione derivative (**2**) showing UV absorption at 282 nm and IR bands at 1685, 1648 and 1603 cm^{-1}, thus relating castanopsin to a β-amyrin derivative similar to saikogenin B [2]. On the basis of UV absorption and formation of a dienedione the position of the diene chromophore was fixed as $\Delta^{9(11),12(13)}$.

The MS showed a prominent fragment ion at *m/e* 255, derived from rings C, D and E, which eliminated the presence of the hindered hydroxy [3–6] group in rings C, D and E. Thus it could be located at either C-6 or C-7. The $W_{\frac{1}{2}}$ of the geminal proton at δ 4.14 ppm corresponding to the hindered hydroxyl group was of the order of 7 Hz which was compatible with its equatorial configuration and placement at C-7. The relative hindrance to acylation of the axial OH further confirmed this assignment.

The stereochemistry of the OH at C-3 was established from the NMR spectrum. The carbinolic proton at δ 3.78 ppm in castanopsin appeared as a quartet (J_{aa} = 10 Hz, J_{ae} = 6.5 Hz) due to coupling with adjacent methyl-

* CDRI Communication No. 2332.

ene protons and compatible only with the (α) axial proton; the hydroxyl would therefore be β. On the basis of these data, the structure of castanopsin was elucidated as olean-9,12-diene-3β,7α-diol (**1a**). This is one of the rare pentacyclic triterpenoids found in nature having a homoannular diene system. So far only three such triterpenes with a homoannular diene system, saikogenin B [2], echinatic acid [7, 8], isomacedonic acid [9], are known in nature.



2

EXPERIMENTAL

Mps are uncorr. NMR spectra were measured in $CDCl_3$ with TMS as int. stand. In all cases, TLC spots on Si gel plates were developed with 1% $CeSO_4$ in 2 N H_2SO_4

Castanopsin. Mp 224–28°, $[\alpha]_D$ + 289 (*c*, 2.06 $CHCl_3$) λ UV λ_{max}^{MeOH}: 286 nm (log ε 3.9; IR ν_{max}^{KBr} cm^{-1}: 3575, 3290, 1630, 1375, 1365, 1065, 1050, 1035, 987, 835. NMR δ 0.83 (3H, *s*, Me) 0.09 (6H, *s*, 2 × Me), 1.03, 1.06, 1.10, 1.20, 1.26 (3H, each *s*, 5 × Me), 3.78 (1H, *q*, J = 6.5, 10 Hz) CHOH), 4.14 (1H, $W_{\frac{1}{2}}$ = 7 Hz, CHOH), 5.53, 5.71 (2H, *d*, J = 6 Hz —C=CH—CH=C—). MS (*m/e*): 440 (M^+), 422, 404, 286, 268, 255, 235, 205, 189, 183. (Found .C, 81.75, H 10.97 $C_{30}H_{48}O_2$ requires C, 81.81; H 10.99%).

Castanopsin monoacetate. Castanopsin (45 mg) was reacted for 18 hr with Ac_2O (0.4 ml) and dry C_5H_5N (0.4 ml) at 0° and worked up as usual. The derivative (46 mg) was crystallised from MeOH, mp 184–5° IR ν_{max}^{KBr} cm^{-1}: 3320, 1020 (OH), 1730, 1240. NMR: δ 0.83–1.2 (24H, 8 × Me), 2.00 (3H, *s*, OCOMe), 4.14 (1H, *t*, CHOH), 5.02 (1H, *q*, CHOAc), 5.5, 5.68 (2H, *dd*, J = 6 Hz, olefinic H).

Castanopsin diacetate. Castanopsin (48 mg) was mixed with AC_2O (0.5 ml) and dry C_5H_5N (0.5 ml) and heated on a water bath for 3 hr. After working up, the residue (50 mg) gave a colourless powder from dilute EtOH, mp 130–2°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1250 (OCOMe), 840, 820. NMR: δ 0.9 (9H, *s*, 3 × Me), 0.98, 1.03, 1.1 (9H, each *s*, 3 × Me), 1.2 (6H, *s*, 2 × Me), 2.00, 2.03 (6H, each *s*, 2 × OCOMe), 4.93 (1H, *t*, J = 8 Hz, CHOAc), 5.36 (1H, *t*, J = 3 Hz, CHOAc), 5.48 (2H, olefinic H). When castanopsin was reacted for 18 hr with Ac_2O and C_5H_5N at room temp., mono- and diacetates were formed in almost equal ratio.

SeO_2 oxidation of castonopsin diacetate. The diacetate (30 mg) was refluxed with freshly sublimed SeO_2 (30 mg) in HOAc (3 ml) for 3 hr. After work up, the residue gave a colourless powder (17 mg) from dilute EtOH, mp 190–2°. UV λ_{max}^{MeOH}: 282 nm (log ε 4.00). IR ν_{max}^{KBr} cm^{-1} 2940, 2860, 1730, 1245 (OCOMe), 1685, 1648, 1603 (dienedione), 1450, 1370, 1360.

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CROSS CONJUGATED TERPENOID KETONES: A NEW GROUP OF PLANT GROWTH REGULATORS

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Key Word Index—Plant growth regulators, terpenoid ketones; zerumbone.

The current trend in the researches on plant growth regulators is to clarify the structural specificity required for hormonal activity [1, 2]. The biological potentialities of terpenoids in general and of terpenoid lactones in particular as plant growth regulators are being explored intensively [3].

It had been established that the physiological activity of the terpenoid lactones is due to the conjugated exo-methylene moiety which is most probably essential [4]. Previous work from our laboratory showed that some terpenoid γ-lactones in which conjugation is of a different type [5] are physiologically more active than α-methylene-γ-lactones.

We have carried out extensive screening of terpenoids as plant growth regulators is an attempt to relate structure with growth activity. In this communication we