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STRUCTURE OF OPUNTIOL, A CONSTITUENT OF *OPUNTIA ELATIOR*

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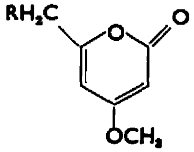
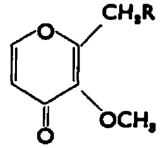
Abstract—Opuntiol, a crystalline constituent of *Opuntia elatior* has been shown to be 2-hydroxymethyl-4-methoxy-α-pyrone.

OPUNTIA ELATIOR (Cactaceae) grows in waste places in most parts of India. From the petroleum ether extract of the dried, powdered plant material β-sitosterol was isolated. Further extraction with chloroform yielded a crystalline compound, m.p. 180–181°, named Opuntiol.

Opuntiol (I), $C_7H_8O_4$ (mol. wt. by mass spectrum, 156) contains one methoxyl group (Zeisel) and an alcoholic hydroxyl group. It forms a monoacetate, $C_9H_{10}O_5$ (II), m.p. 110–111°. Both opuntiol and its acetate exhibit an absorption maximum at 280 mμ. The IR spectrum of opuntiol had bands at 3395, 1720, 1700, 1640 and 1570 cm^{-1} and the acetate at 1735, 1720, 1700, 1650 and 1570 cm^{-1}. (Figs. 1 and 2). On the basis of the UV and IR absorption data, the possibility of opuntiol being 2-hydroxymethyl-3-methoxy-γ-pyrone (III) was first considered. The compound IV was synthesized from maltol methyl ether (V) by effecting side-chain bromination through N-bromosuccinimide and conversion of the bromomethyl compound (VII) to the acetate. However, compound IV synthesized in this fashion was completely different from opuntiol acetate. A comparison of the NMR spectra of the synthetic compound IV (Fig. 3) and opuntiol acetate II (Fig. 4) was most informative. The former had signals at τ 7·88 (—$OCOCH_3$), 6·04 (OCH_3), 4·89 (—CH_2OCOCH_3) and two doublets centred at τ 4·6 and 2·3 (J = 6 c/s) ascribed to the α and β protons of the γ-pyrone system. Opuntiol acetate had signals at τ 7·85 (—$OCOCH_3$), 6·15 (OCH_3), 5·15 (—CH_2OCOCH_3) and two doublets centred at τ 4·5 and 3·95 (J = 2 c/s). The J value was of such an order that it could not be ascribed to adjacent vinyl protons, but was indicative of a 1:3 relationship between these protons. A closer scrutiny of the UV data (Table) indicates that the spectrum of opuntiol is more akin to that of an α- rather than a γ-pyrone. From biogenetic considerations and compatibility with NMR and UV spectra, opuntiol is likely to be 2-hydroxymethyl-4-methoxy-α-pyrone (I). This was proved in the following way. Opuntiol was refluxed



I R = OH
II R = $OCOCH_3$
VI R = H



III R = OH
IV R = $OCOCH_3$
V R = H
VII R = Br

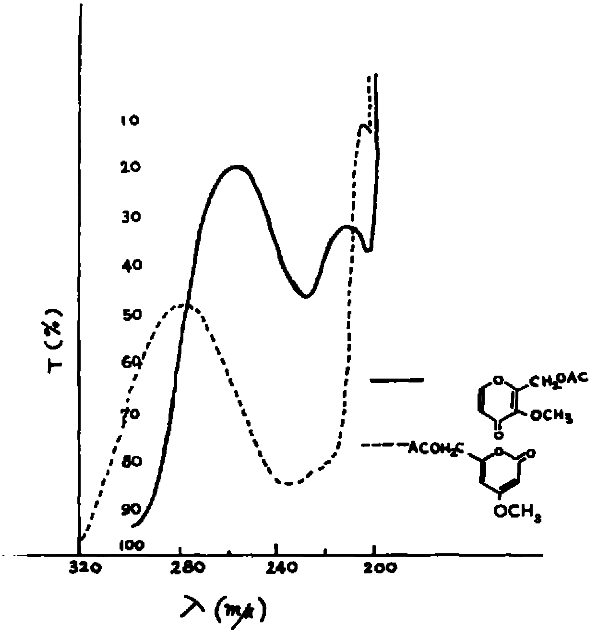

10
20
30
40
50
60
70
80
90
100
T (%)
320
280
240
200
λ (mμ)
CH2OAC
OCH3
O
ACOH2C
O
OCH3

FIG. 1

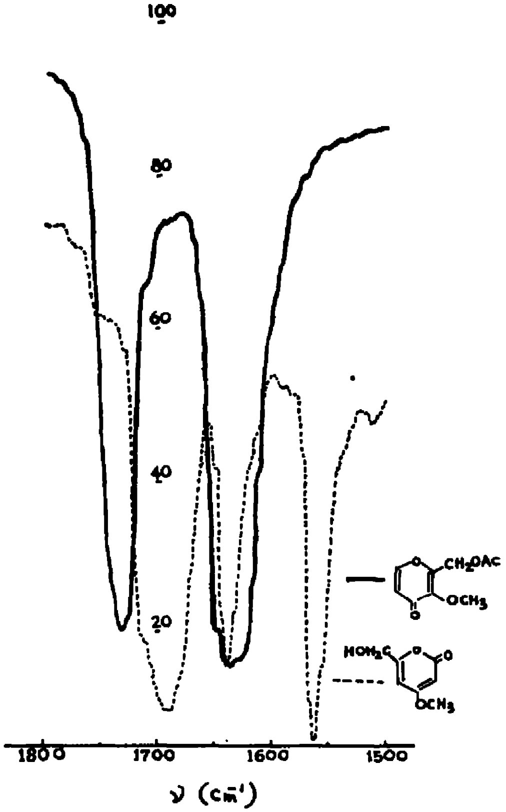

100
80
60
40
20
1800
1700
1600
1500
ν (cm⁻¹)
CH2OAC
OCH3
O
HOH2C
O
OCH3

FIG. 2

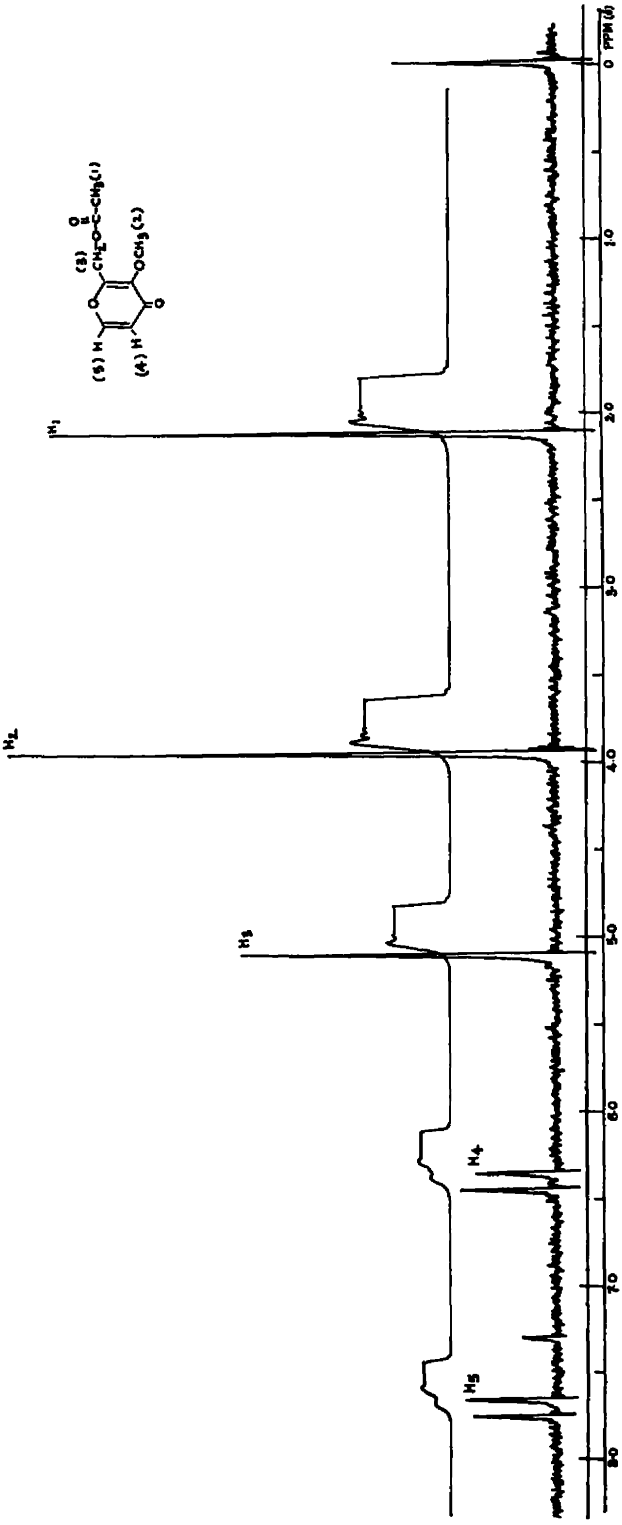

0 PPM (δ)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
H1
H2
H3
H4
H5
(5) H
(4) H
(3)
O
CH2-O-C-CH3(1)
OCH3(2)

FIG. 3

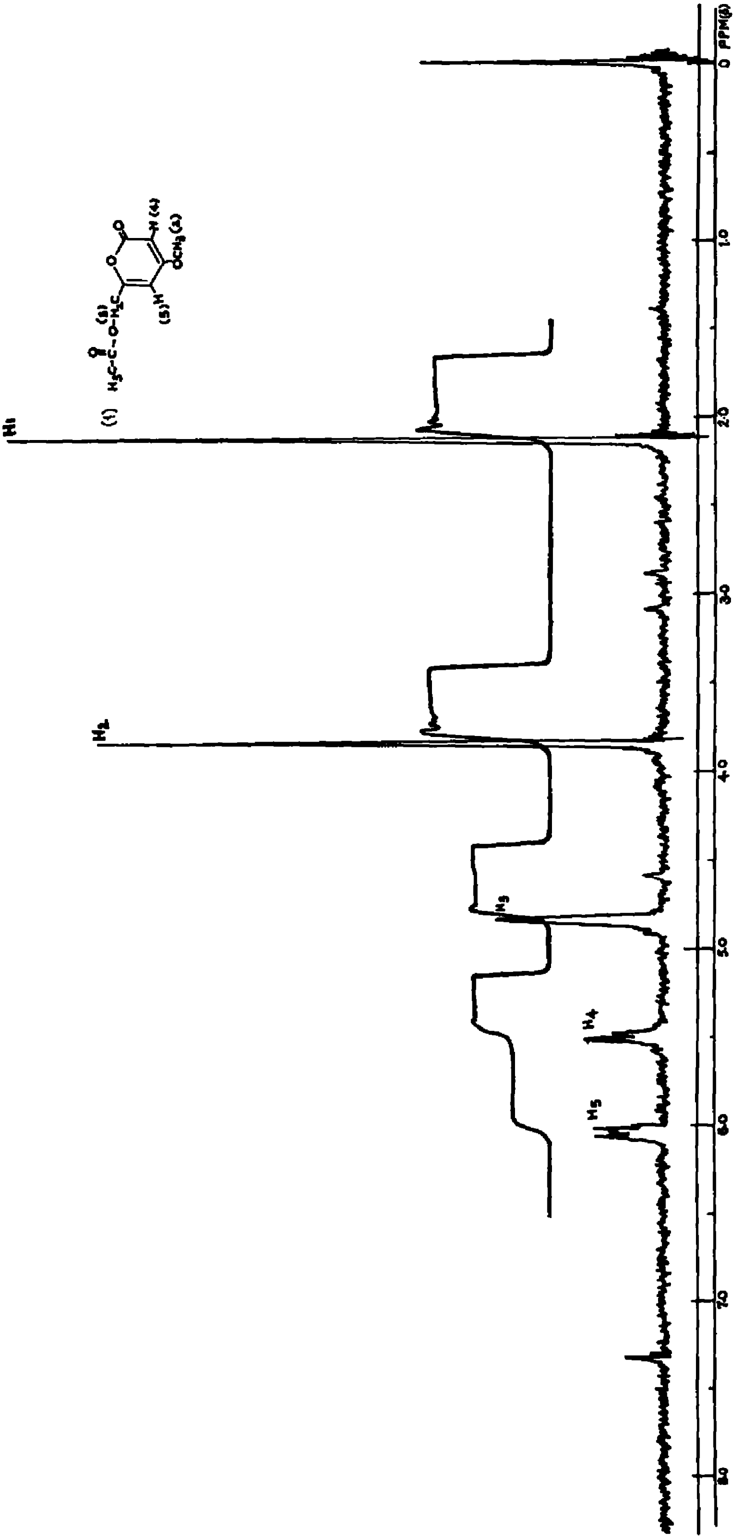
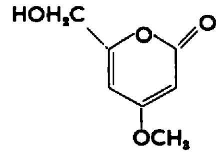
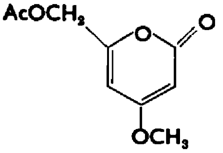
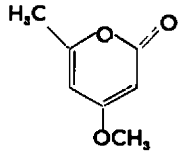
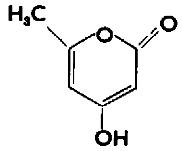
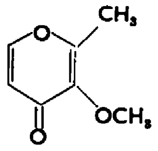
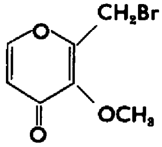
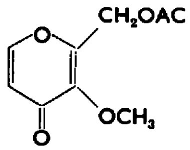
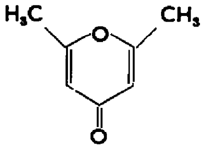

(1) H3C-C-O-H2C (3)
H (4)
OCH3 (2)
(5) H
H1
H2
H3
H4
H5
0 PPM(δ)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

FIG. 4

Compound	Reference	λ_{max} (mμ)	ϵ_{max}	ν_{max} (cm^{-1})
		280	7033	1720, 1700, 1640, 1570
		280	5199	1735, 1720, 1700 1650 1570,
	1	280	5879	1715, 1700, 1640, 1560
	2	280	7404	1715, 1700, 1640, 1560
	3	256 208	8020 8020	1645
		268 220	8385 5765	1640
		256 208	8792 6365	1730, 1640
	4	246	14670	

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[1] D. Herbest, W. B. Mors, O. R. Gottlreb, C. Djerassi, *J. Amer. Chem. Soc.* **81**, 2427 (1959).

[2] J. Collie, *J. Chem. Soc.* **59**, 609 (1891).

[3] Peratoner and Tamburello, *Chem. Zent.* **11**, 680 (1905).

[4] J. Collie, *J. Chem. Soc.* **59**, 620 (1891).

with thionyl chloride to yield a crystalline chloro compound, which on reduction with zinc dust and acetic acid yielded the desoxy compound $C_7H_8O_3$ m.p. 85–86°, λ_{max} 280 mμ, ν_{max} 1715, 1700, 1640 and 1560 cm^{-1}, which proved to be identical (m.p.; m.m.p.; IR spectra) with an authentic sample of 2-methyl-4-methoxy-α-pyrone (VI) prepared from dehydroacetic acid.[1] Opuntiol is the third naturally occurring α-pyrone and its occurrence in a cactus species is interesting since only complex triterpenoids have been reported from many species of Mexican cactus.[5] The biogenetic derivation of opuntiol through three acetate units is obvious.

EXPERIMENTAL

M.ps were determined on a Kofler block. IR and UV spectra were determined in chloroform and cyclohexane solutions respectively. NMR. spectra were taken in $CDCl_3$ at 60 MC.

Extraction. Finely powdered *Opuntia elatior* whole plant (7·5 kg) was extracted successively with hexane, chloroform and methanol at room temp. From the hexane extract a gum (40 g) was obtained which was chromatographed over alumina (400 g). Elution with chloroform afforded a colourless crystalline compound which upon crystallization from acetone–methanol yielded colourless needles m.p. 135° alone or when mixed with an authentic sample of β-sitosterol. The identity was further proved by comparison of IR spectra and also by thin layer chromatography.

The chloroform extract mentioned above, on evaporation yielded a greenish gum (70 g). This was taken up in small amount of chloroform and adsorbed on a column of neutral alumina (400 g) and eluted with chloroform followed by methanol. The latter eluate (300 ml) on concentration yielded a solid contaminated with chlorophyll. It was dissolved in acetone, refluxed with decolourizing charcoal and filtered hot. The filtrate when concentrated yielded a colourless crystalline compound m.p. 175–180°. Repeated crystallization from acetone yielded rhombic crystals of opuntiol (I) m.p. 180–181° (3·8 g), λ_{max} 280 mμ (ϵ, 7033), ν_{max} 1720, 1700, 1640 and 1570 cm^{-1}. (Found: C, 53·99; H, 5·40; OCH_3, 20·01. $C_7H_8O_4$ requires: C, 53·84; H, 5·16; OCH_3, 19·87%). The acetate, prepared in the usual way (acetic anhydride–pyridine), was crystallized from acetone–hexane as colourless needles m.p. 110–111°, λ_{max} 280 mμ (ϵ, 5199), ν_{max} 1735, 1720, 1700, 1650, 1570 cm^{-1}. (Found: C, 54·39; H, 5·04; $C_9H_{10}O_5$ requires: C, 54·54; H, 5·09%).

Desoxyopuntiol (VI). The alcohol (I ; 200 mg) in chloroform solution (1·5 ml) was refluxed with thionyl chloride (0·5 ml) for 30 min. The solvent was then removed under red. press. yielding a crystalline compound which gave positive Beilstein test. The above chloro compound was shaken with glacial acetic acid (1·5 ml) and Zn dust (350 mg) for ½ hr and then filtered. Hydrogen sulphide was passed through the filtrate and the precipitated ZnS filtered off. Acetic acid was removed from the filtrate under red. press. and the residue extracted with chloroform. On evaporation of the solvent a brownish solid was obtained which sublimed at 90°/1 mm as colourless needles. It was recrystallized twice from cyclohexane and again sublimed as above to obtain colourless needles m.p. 84–85° alone or when mixed with an authentic sample of VI; λ_{max} 280 mμ (ϵ, 5879), ν_{max} 1715, 1700, 1640, 1560 cm^{-1}. (Found: C, 60·30; H, 5·57. $C_7H_8O_3$ requires: C, 59·99; H, 5·75%).

2-*Bromomethyl*-3-*methoxy*-γ-*pyrone* (VII). Maltol methyl ether (6 g) was refluxed with recrystallized N-bromosuccinimide (10 g) in dry carbon tetrachloride (300 ml) for 14 hr. The reaction mixture was filtered. Evaporation of the filtrate yielded an oil which distilled at 120° (1 mm) as a brown liquid, λ_{max} 268, 220 mμ (ϵ, 8385 and 5765). (Found: C, 38·96; H, 3·77. $C_7H_7O_3Br$ requires: C, 38·60; H, 3·42%). The compound is irritant and lachrymatory.

2-*Acetoxymethyl*-3-*methoxy*-γ-*pyrone* (IV). The above bromo compound (VII; 2·5 g) was refluxed with fused sodium acetate (2·5 g) and acetic anhydride (25 ml) for 1 hr. The reaction mixture was cooled, poured on crushed ice and extracted with chloroform. The chloroform extract was washed with $NaHCO_3$ aq, dried (Na_2SO_4), filtered and distilled over neutral alumina (20 g) and eluted with benzene. The earlier fractions on evaporation gave a solid which crystallized from pentane as

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[5] C. Djerassi, *Festschrift Arthur Stoll* 330 (1957).

colourless needles, which was further purified by sublimation at 80°/1 mm. m.p. 70–72°, λ_{max} 256, 208 mμ (ϵ, 8792 and 6363 respectively), ν_{max} 1735, 1640 cm^{-1}. (Found: C, 54·99; H, 5·31. $C_9H_{10}O_5$ requires: C, 54·54; H, 5·09%).

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