neo-clerodane [3] absolute configuration of salvifaricin (**4**) was established by the fact that treatment of salvifarin (**3**) with sodium iodide-*p*-toluensulfonic acid in acetonitrile solution [4] yielded a compound identical in all respects (mp, mmp, $[\alpha]_D$, IR, ^{1}H NMR, mass spectra, TLC) with natural salvifaricin (**4**).

EXPERIMENTAL

For the isolation of salvifaricin (**4**) from *Salvia farinacea* and its spectroscopic data see ref. [1]. ^{1}H NMR spectra were measured at 80 MHz in $CDCl_3$ soln with TMS as internal standard. The proton NOE measurements were made by the FT difference method with the decoupler operating in the gated mode.

Salvifaricin (**4**) *from salvifarin* (**3**). A mixture of salvifarin (**3**, 36 mg, 0.1 mmol), NaI (0.5 mmol) and *p*-toluensulfonic acid (0.3 mmol) in dry acetonitrile (1 ml) was stirred at room temp. for 1 hr. Work-up in the usual manner [4] yielded, after preparative TLC purification, 28 mg of a compound, mp 213–215° (from MeOH), $[\alpha]^{22}_D - 153.7°$ ($CHCl_3$; *c* 0.37), identical in all respects (mmp, IR, ^{1}H NMR, mass spectra, TLC) with salvifaricin (**4**, mp 214–215°, $[\alpha]^{20}_D - 155.2°$) [1].

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THE STRUCTURE OF SAGITTARIOL*

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Key Word Index—*Sagittaria sagittifolia*; Alismataceae; sagittariol; oxodeoxysagittariol; methyl hardwickiate; hardwickiol; kolavenic acid; methyl floribundate; cistodiol; ^{13}C NMR spectra.

Abstract—Sagittariol, heretofore considered to be 17-hydroxymanool, has been shown to incorporate an A-B *cis* clerodane skeleton on the basis of a ^{13}C NMR spectral analysis of several labdanic and clerodanic diterpenes.

In a recent study of sagittariol, a chemical constituent of the Indian aquatic herb *Sagittaria sagittifolia* L., the compound was assigned the labdane structure **1a**, on the basis of ^{1}H NMR (60 MHz) and mass spectral data and some chemical transformations [1]. However, a NMR reinvestigation now has yielded evidence incompatible with this formulation. Firstly, a ^{1}H NMR spectral analysis at 360 MHz has revealed the diterpene's four methyl groups as three singlets and one doublet, indicative of a methyl function residing on a methine. Secondly, ^{13}C NMR spectral comparison of sagittariol with its cogener oxodeoxysagittariol [J. S. Tandon, unpublished observations], initially formulated as **1b**, showed the strongly deshielded keto-α-carbon of the latter to be a methylene instead of a methine. In addition, the chemical shifts of the octalone carbons of the latter ketone were strikingly different from those of hedychenone (**2**) [2], an oxolabdane of related structure.

Sagittariol and its 14,15-dihydro product exhibited carbon signals characteristic of the methylvinylcarbinol terminus of the C-9 side-chain of manool [3]. Comparison of the carbon shifts of the nuclear double bond and the hydroxymethyl group of sagittariol with those of the product of acetylation of the primary alcohol moiety revealed Δδ values indicative of a second allyl alcohol unit in the diterpene [4]. Whereas all functional groups had been recognized correctly previously [1], they could not

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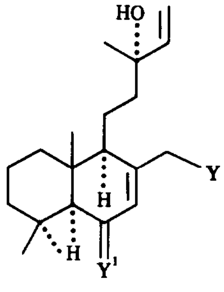
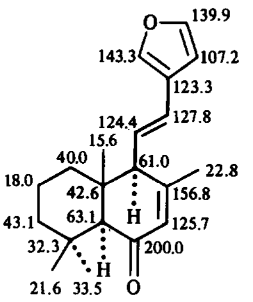
*Part LXXX in the series "Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances". For part LXXIX see Pinheiro, M. L. B., Wolter Filho, W., da Rocha, A. I., Porter, B. and Wenkert, E. (1983) *Phytochemistry* **22**, 2320.



1a Y=OH, $Y^1=H_2$
1b Y=H, Y^1=O



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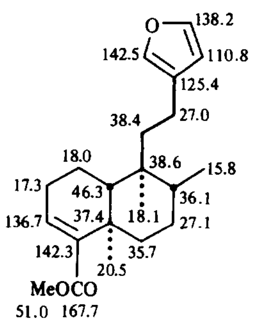

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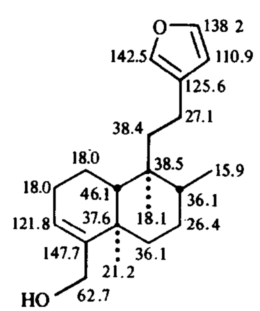

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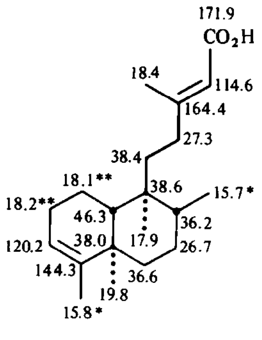

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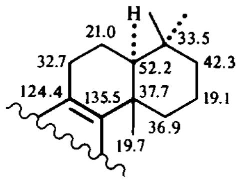

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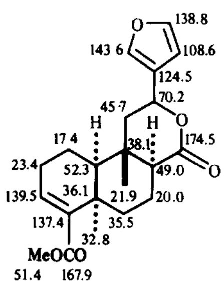
Table 1. ^{13}C chemical shifts of sagittariol derivatives (**10**)*

Carbon	**10a**	**10b**	**10c**†	**10d**
1	17.2	17.2	17.0	35.0
2	23.6	23.6	23.7	200.8
3	124.7	124.1	128.9	128.2
4	143.0	142.8	137.9	168.3
5	36.0	36.0	36.0	39.1
6	36.7	36.7	37.1	36.7
7	28.8	28.8	28.5	28.2
8	37.2	37.1	37.1	36.5
9	39.6	40.0	39.5	39.8
10	44.9	44.9	44.7	46.9
11	31.4	31.4	31.3	30.3
12	34.9	33.5	34.8	35.3
13	73.3	73.0	73.1	73.0
14	144.9	33.5	144.8	144.6
15	111.7	8.0	111.5	111.9
16	27.6	26.4	27.5	27.4
17	15.7	15.8	15.7	15.9
18	64.5	64.1	66.4	20.5
19	34.9	34.7	34.4	32.0
20	17.3	17.4	17.2	19.2

*In δ-values (ppm) downfield from TMS; δ(TMS) = δ$(CDCl_3)$ + 76.9 ppm.

†Acetate δ (CO) = 170.5 ppm and δ (Me) = 21.0 ppm.



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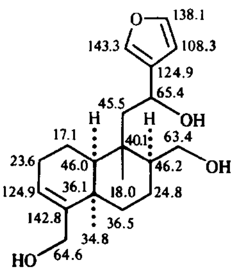

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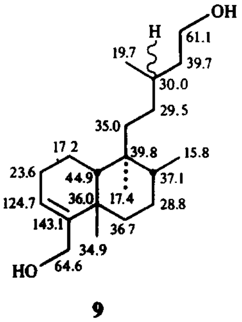

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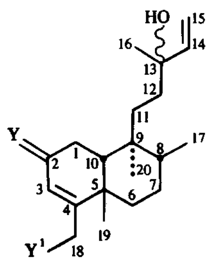

10 a $Y=H_2$, Y^1=OH
10 b $Y=H_2$, Y^1=OH, 14, 15-dihydro
10 c $Y=H_2$, Y^1=OAc
10 d Y=O, Y^1=H

be incorporated in a labdane skeleton. The presence of a methine-attached methyl group and its frequent appearance at C-8 among clerodane-like diterpenes suggested that sagittariol might belong to the latter class of natural products. For this reason it became necessary to acquire ^{13}C NMR data on selected examples of such compounds.

The ^{13}C NMR spectra of the methyl ester (**3**) and lithium aluminum hydride reduction product (**4**) of hardwickiic acid [5] as well as kolavenic acid (**5**) [5] were analysed on the basis of standard chemical shift theory and by the use of the shifts of the ring B and A carbons of the $\Delta^{8(9)}$-pimaradienes (**6**) [6] for the assignment of the ring A and B carbons of the clerodanes, respectively. Even though many of the ring B carbons of these substances showed shifts similar to some of sagittariol and their equatorial 8-methyl resonances were identical with those of the latter, the non-identity of the ring A carbon shifts of hardwickiol (**4**) and sagittariol indicated the need for one more structural change, but probably within the clerodane skeleton. As a consequence a ^{13}C NMR spectral study of a few selected A-B *cis* clerodanes was undertaken.

A ^{13}C NMR spectral analysis of the methyl ester (**7**) and lithium aluminum hydride reduction product (**8**) of floribundic acid [7] as well as cistodiol (**9**) [8] yielded the shifts depicted on the formulae. Three interesting facts emanated from these data: (a) the 8-methyl group of cistodiol (**9**) being equatorial; (b) the three substances maintaining the A-B *cis* steroid conformation in solution; (c) the chemical shifts of the nuclear carbons and one-carbon side-chains of cistodiol (**9**) being nearly identical with like carbon sites of sagittariol. Thus the relative configuration of sagittariol is as pictured in structure **10a**. The carbon shifts of the diol and its derivatives are listed in Table 1.

EXPERIMENTAL

The ^{1}H NMR spectrum of sagittariol (**10a**) in CDCl$_3$ soln with TMS as int. standard ($\delta = 0$) was recorded on a 360 MHz spectrometer equipped with an Oxford magnet and a computer system. The ^{13}C NMR spectra were obtained on a wide-bore, broad-band spectrometer, operating with an Oxford magnet at 50.31 MHz in the Fourier transform mode. The carbon shifts on formulas **2**–**9** are in δ-values (ppm) downfield from TMS; δ(TMS) = δ(CDCl$_3$) + 76.9 ppm. The asterisked shifts on formula **5** may be interchanged.

Sagittariol (**10a**). ^{1}H NMR: δ 0.73 (3H, *d*, J = 7 Hz, 8-Me), 0.76 (3H, *s*, 9-Me), 1.11 (3H, *s*, 5-Me), 1.29 (3H, *s*, 13-Me), 1.42 (1H, *m*, H-8), 4.06, 4.10, 4.18, 4.21 (2H, AB *dd*, 2H-18), 5.0–5.9 (3H, *m*, vinyl Hs), 5.61 (1H, *br s*, H-3).

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PHYSCION-8-*O*-GENTIOBIOSIDE FROM *RHAMNUS VIRGATA*

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Key Word Index—*Rhamnus virgata*; Rhamnaceae; physcion; physcion-8-*O*-gentiobioside; anthraquinone.

Abstract—A new anthraquinone diglucoside isolated from *Rhamnus virgata* has been shown to be physcion-8-*O*-β-gentiobioside on the basis of spectral and other evidence.

INTRODUCTION

The stems of *Rhamnus virgata* L. afforded a new compound, the colour reactions and solubility properties of which indicated it to be a quinone glycoside. Its IR spectrum indicated the presence of hydroxyl and chelated and non-chelated carbonyls. On hydrolysis with Kiliani reagent [1], it gave an aglycone which was identified as physcion from spectral properties and direct comparison with authentic physcion, and glucose as the only identifiable sugar. In the ^{1}H NMR spectrum of the peracetate, there were signals for a phenolic acetoxyl and an aromatic methyl (δ 2.45), six alcoholic acetoxyls (δ 2.00) and an alcoholic acetoxyl (1.80) indicating the presence of a disaccharide moiety attached to the hydroxyl group at either C-1 or C-8 of the aglycone. The aromatic region had two *meta* coupled doublets (δ 7.50 and 6.88, J = 2.5 Hz each) arising from the resorcinol ring of the aglycone and two broad singlets (δ 7.92 and 7.18) assignable to two

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