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ψ-ESTERS OF DEPSIDONES WITH A LACTOLE RING*

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Key Word Index—ψ-Esters; depsidones; 8′-*O*-methylstictic acid; 8′-*O*-ethylstictic acid; 8′,9′-di-*O*-ethylsalazinic acid.

Abstract—The reaction of stictic, norstictic and salazinic acids with methanol, ethanol and tert-butanol has been investigated. 8′-*O*-Methylstictic acid is identical with methylstictic acid from *Lobaria oregana*. Ingolfdottir's vesuvianic acid from *Stereocaulon vesuvianum* and Handong's cetrariastrumin from *Cetrariastrum nepalensis* have been shown to be 8′-*O*-ethylstictic acid and 8′,9′-di-*O*-ethylsalazinic acid, respectively, by reaction of stictic and salazinic acids with ethanol.

INTRODUCTION

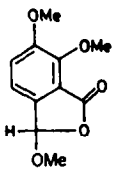
In continuation of our work on the chemistry of lichen substances, we have investigated the reaction of methanol, ethanol and tert-butanol with stictic, norstictic and salazinic acids, depsidones with a lactole ring in the A-part of the molecule. The lactole structure is tautomeric with the *o*-aldehyde carboxylic acid structure and hence two esters are possible: the ψ-ester and the normal ester, as demonstrated for the first time by Wegscheider [1, 2] who showed that opianic acid (2,3-dimethoxy-6-formylbenzoic acid) gave on heating with methanol the ψ-ester (A) in the absence of mineral acids and the normal ester (B) in the presence of mineral acids.

RESULTS AND DISCUSSION

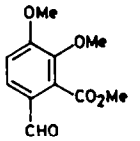
Stictic acid (**1**) gave on boiling with methanol a mixture from which it was possible to isolate 8′-*O*-methylstictic acid (**2**) identical (mp, UV, ^{1}H NMR, MS) with methylstictic acid [3] (Table 1). Authentic methylstictic acid isolated from *Lobaria oregana* (Tuck.) Müll. Arg. and an acetone extract of a sample of this lichen kindly provided to us by Dr. J. A. Elix (from the herbarium of Prof. U. Sankawa, Tokyo) gave on TLC one spot of the same R_f value as **2**.

Fractional crystallization of the reaction products of **1** and methanol gave a compound with the ^{1}H NMR properties expected for the 9-dimethylacetal of stictic acid (**3**): δ2.20 (*s*, 3H, 9′-Me), 2.50 (*s*, 3H, 8-Me), 3.17, 3.46 [2 × *s*, 2 × 3H, 9-CH(OMe)$_2$], 3.92 (*s*, 3H, 4-OMe), 5.98 [*s*, 1H, 9-CH(OMe)$_2$], 6.65 (*d*, J = 8 Hz, 1H, 8′-H), 7.00 (*s*, 1H, 5-H), 8.25 (*d*, J = 8 Hz, 1H, 8′-OH), 10.47 (*s*, 1H, 2′-OH) (see Table 2).

On treatment of **2** with acetic anhydride/pyridine 2′-*O*-acetyl-8′-*O*-methylstictic acid (**4**) was formed while reaction of **3** with acetic anhydride/sulphuric acid gave a compound identical with 9,9,2′,8′-tetra-*O*-acetylstictic acid (**5**). Methylation of stictic acid with methyl iodide and



A



B

* Part 145 in the series "Lichen Substances". For part 144 see Huneck, S. *et al.* (1986) *Phytochemistry* **25**, 453.

Table 1. Comparison of the physical and spectroscopic data of methylstictic acid from *Lobaria oregana* with those of 8′-*O*-methylstictic acid

	Methylstictic acid of Shimada *et al.* [3]	8′-*O*-Methylstictic acid
Mp	250–251° (dec.)	248–249°
UV (λ_{max})	238 (4.62), 312 (3.77) (in EtOH)	218 (4.83), sh 260 (4.30), sh 310 (3.90) (in MeOH)
^{1}H NMR (DMSO-d_6)	2.22 (*s*, 3H), 2.48 (*s*, 3H), 3.44 (*s*, 3H) 3.91 (*s*, 3H), 6.44 (*s*, 1H), 7.08 (*s*, 1H) 10.3 (*s*, 1H), 10.39 (*s*, 1H) (100 MHz)	2.21 (*s*, 3H), 2.49 (*s*, 3H), 3.46 (*s*, 3H), 3.92 (*s*, 3H), 6.46 (*s*, 1H), 7.08 (*s*, 1H), 10.40 (*s*, 1H) (200 MHz)
MS, *m/z*	400, 368, 340, 193, 191	400, 368, 355, 340, 325, 312, 297, 285, 270, 259, 193, 191, 164, 148

Table 2. ^{1}H NMR data of compounds **1–11**, **13**, **15–30**, **32** and norstictic acid pentaacetate

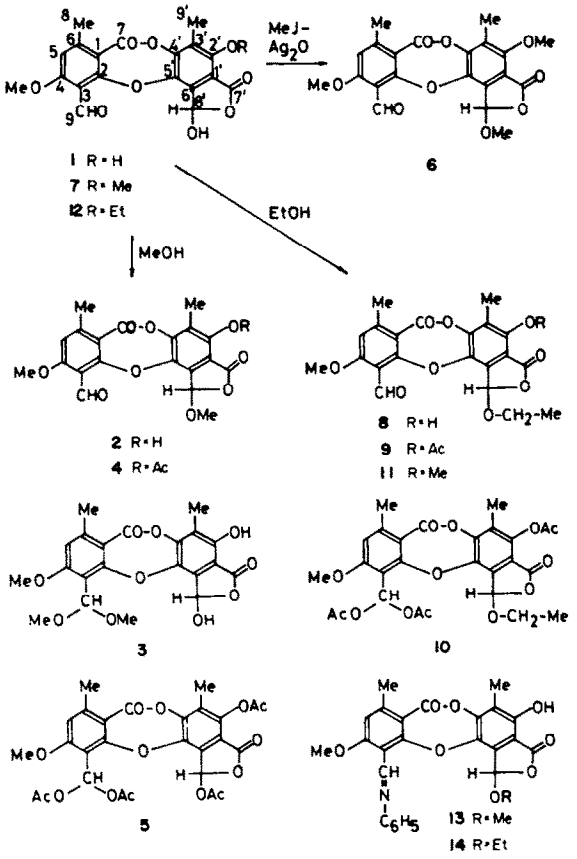
Compound No.	MHz	Solvent	Chemical shifts and coupling constants
1	60	DMSO-d_6	2.20 (*s*, 3H, 9′-Me), 2.50 (*s*, 3H, 8-Me), 3.91 (*s*, 3H, 4-OMe), 6.62 (*s*, 1H, 8′-H), 7.07 (*s*, 1H, 5-H), 10.39 (*s*, 1H, 9-H)
2	200	DMSO-d_6 + D_2O + D_2SO_4	2.21 (*s*, 3H, 9′-Me), 2.49 (*s*, 3H, 8-Me), 3.46 (*s*, 3H, 8′-OMe), 3.92 (*s*, 3H, 4-OMe), 6.46 (*s*, 1H, 8′-H), 7.08 (*s*, 1H, 5-H), 10.40 (*s*, 1H, 9-H)
3	200	DMSO-d_6	2.20 (*s*, 3H, 9′-Me), 2.50 (*s*, 3H, 8-Me), 3.17, 3.46 [2 × *s*, 2 × 3H, 9-CH (OMe)$_2$], 3.92 (*s*, 3H, 4-OMe), 5.98 [*s*, 1H, 9-CH(OMe)$_2$], 6.65 (*d*, J = 8 Hz, 1H, 8′-H), 7.00 (*s*, 1H, 5-H), 8.25 (*d*, J = 8 Hz, 1H, 8′-OH), 10.47 (*s*, 1H, 2′-OH)
4	200	$CDCl_3$	2.29 (*s*, 3H, 9′-Me), 2.43 (*s*, 3H, 2′-OAc), 2.57 (*s*, 3H, 8-Me), 3.68 (*s*, 3H, 8′-OMe), 3.99 (*s*, 3H, 4-OMe), 6.32 (*s*, 1H, 8′-H), 6.78 (*s*, 1H, 5-H), 10.50 (*s*, 1H, 9-H)
5	200	$CDCl_3$	2.09, 2.18, 2.20 (3 × *s*, 3 × 3H, 3 × –OAc), 2.30 (*s*, 3H, 9′-Me), 2.44 (*s*, 3H, –OAc), 2.52 (*s*, 3H, 8-Me), 3.93 (*s*, 3H, 4-OMe), 6.73 (*s*, 1H, 5-H), 7.89 (*s*, 1H, 8′-H), 8.05 (*s*, 1H, 9-H)
6	200	$CDCl_3$	2.26 (*s*, 3H, 9′-Me), 2.51 (*s*, 3H, 8-Me), 3.48 (*s*, 3H, 8′-OMe), 3.93, 3.94 (2 × *s*, 2 × 3H, 2 × –OMe), 6.52 (*s*, 1H, 8′-H), 7.14 (*s*, 1H, 5-H), 10.42 (*s*, 1H, 9-H)
7	200	$CDCl_3$	2.33 (*s*, 3H, 9′-Me), 2.58 (*s*, 3H, 8-Me), 3.99 (*s*, 3H, 4-OMe), 4.07 (*s*, 3H, 2′-OMe), 6.64 (*s*, 1H, 8′-H), 6.77 (*s*, 1H, 5-H), 10.51 (*s*, 1H, 9-H)
8	100	DMSO-d_6	1.35 (*t*, J = 7 Hz, 3H, –CH$_2$–Me), 2.40 (*s*, 3H, 9′-Me), 2.70 (*s*, 3H, 8-Me), 3.96 (*m*, 2H, –CH$_2$–Me), 4.16 (*s*, 3H, 4-OMe), 6.70 (*s*, 1H, 8′-H), 7.24 (*s*, 1H, 5-H), 10.24 [*s* (*br*), 1H, OH], 10.60 (*s*, 1H, 9-H)
9	200	$CDCl_3$	1.25 (*t*, J = 7 Hz, 3H, –CH$_2$–Me), 2.28 (*s*, 3H, 9′-Me), 2.43 (*s*, 3H, 2′-OAc), 2.57 (*s*, 3H, 8-Me), 3.93 (*m*, 2H, –CH$_2$–Me), 3.99 (*s*, 3H, 4-OMe), 6.41 (*s*, 1H, 8′-H), 6.78 (*s*, 1H, 5-H), 10.53 (*s*, 1H, 9-H)
10	200	$CDCl_3$	1.28 (*t*, J = 7 Hz, 3H, –CH$_2$–Me), 2.12, 2.13 (2 × *s*, 2 × 3H, 2 × –OAc), 2.27 (*s*, 3H, 9′-Me), 2.43 (*s*, 3H, –OAc), 2.53 (*s*, 3H, 8-Me), 3.88 (*m*, 2H, –CH$_2$–Me), 3.95 (*s*, 3H, 4-OMe), 6.74 (*s*, 1H, 8′-H), 6.78 (*s*, 1H, 5-H), 8.14 (*s*, 1H, 9-H)
11	200	$CDCl_3$	1.26 (*t*, J = 7 Hz, 3H, –CH$_2$–Me), 2.33 (*s*, 3H, 9′-Me), 2.57 (*s*, 3H, 8-Me), 3.95 (*m*, 2H, –CH$_2$–Me), 3.98 (*s*, 3H, 4-OMe), 4.05 (*s*, 3H, 2′-OMe), 6.37 (*s*, 1H, 8′-H), 6.75 (*s*, 1H, 5-H), 10.55 (*s*, 1H, 9-H)
13	200	$CDCl_3$	2.29 (*s*, 3H, 9′-Me), 2.50 (*s*, 3H, 8-Me), 3.14 (*s*, 3H, 8′-OMe), 3.86 (*s*, 3H, –4–OMe), 5.72 (*s*, 1H, 8′–H), 6.66 (*s*, 1H, 5-H), 6.94 (*dd*, 1H, 4″-H), 7.03, 7.30 (2 × *d*, 2 × 2H, 2″-, 3″-, 5″-, 6″-H), 7.24 (*s*, 1H, 9-H)
15	60	DMSO-d_6	2.20 (*s*, 3H, 9′-Me), 2.45 (*s*, 3H, 8-Me), 6.83 (*s*, 1H, 8′-H), 6.88 (*s*, 1H, 5-H), 10.48 (*s*, 1H, 9-H)
16	200	DMSO-d_6	2.21 (*s*, 3H, 9′-Me), 2.45 (*s*, 3H, 8-Me), 3.35 (*s*, –OH), 3.42 (*s*, 3H, 8′-OMe), 6.72 (*s*, 1H, 8′-H), 6.88 (*s*, 1H, 5-H), 10.42 (*s*, 1H, 9-H), 11.99 (*s*, 1H, –OH)
17	200	$CDCl_3$	2.31 (*s*, 3H, 9′-Me), 2.39 (*s*, 3H, 4-OAc), 2.44 (*s*, 3H, 2′-OAc), 2.57 (*s*, 3H, 8-Me), 3.54 (*s*, 3H, 8′-OMe), 6.33 (*s*, 1H, 8′-H), 6.96 (*s*, 1H, 5-H), 10.47 (*s*, 1H, 9-H)
18	200	$CDCl_3$	2.09, 2.12 (2 × *s*, 2 × 3H, 2 × –OAc), 2.28 (*s*, 3H, 9′-Me), 2.36, 2.43 (2 × *s*, 2 × 3H, 2 × –OAc), 2.53 (*s*, 3H, 8-Me), 3.57 (*s*, 3H, 8′-OMe), 6.73 (*s*, 1H, 8′-H), 6.95 (*s*, 1H, 5-H), 8.11 (*s*, 1H, 9-H)
19	200	$CDCl_3$	2.22, 2.35 (2 × *s*, 2 × 3H, 2 × –Me), 3.16 (*s*, 3H, 7-OMe), 3.47 (*s*, 3H, 8′-OMe), 5.23 (*s*, 1H, 8′-H), 6.75 (*s*, 1H, 5-H), 10.21 (*s*, 1H, 9-H), 11.95 (*s*, 1H, –OH)
20	200	$CDCl_3$	2.13 (*s*, 3H, –OAc), 2.33 (*s*, 3H, 9′-Me), 2.35, 2.40 (2 × *s*, 2 × 3H, 2 × –OAc), 2.42 (*s*, 3H, 8-Me), 3.19 (*s*, 3H, 8′-OMe), 3.44 (*s*, 3H, 7-OMe), 5.50 (*s*, 1H, 8′-H), 6.90 (*s*, 1H, 5-H), 10.20 (*s*, 1H, 9-H)
21	200	$CDCl_3$	2.26 (*s*, 3H, 9′-Me), 2.36 (*s*, 3H, 8′-Me), 2.54 (*s*, 3H, 8-Me), 3.77, 3.82, 3.87, 3.92 (4 × *s*, 4 × 3H, 4 × –OMe), 4.89 (*s*, 1H, 8′-OH), 6.65 (*s*, 1H, 5-H), 10.33 (*s*, 1H, 9-H)
22	100	DMSO-d_6	1.31 (*t*, J = 7 Hz, 3H, –CH$_2$–Me), 2.44 (*s*, 3H, 9′-Me), 2.68 (*s*, 3H, 8-Me), 3.90 (*m*, 2H, –CH$_2$–Me), 6.98 (*s*, 1H, 8′-H), 7.05 (*s*, 1H, 5-H), 10.62 (*s*, 1H, 9-H)

23	200	$CDCl_3$	1.23 (*t*, J = 7 Hz, 3H, –CH_2–Me), 2.31 (*s*, 3H, 9′-Me), 2.39, 2.44 (2 × *s*, 2 × 3H, 2 × –OAc), 2.58 (*s*, 3H, 8-Me), 3.87 (*m*, 2H, –CH_2–Me), 6.38 (*s*, 1H, 8′-H), 6.96 (*s*, 1H, 5-H), 10.54 (*s*, 1H, 9-H)
24	200	$CDCl_3$	1.27 (*t*, J = 7 Hz, 3H, –CH_2–Me), 2.09, 2.10, 2.27 (3 × *s*, 3 × 3H, 3 × –OAc), 2.36 (*s*, 3H, 9′-Me), 2.43 (*s*, 3H, –OAc), 2.53 (*s*, 3H, 8-Me), 3.91 (*m*, 2H, –CH_2–Me), 6.76 (*s*, 1H, 8′-H), 6.95 (*s*, 1H, 5-H), 8.10 (*s*, 1H, 9-H)
25	60	DMSO-d_6	2.45 (*s*, 3H, 8-Me), 4.61 (*s*, 2H, 9′-CH_2–), 6.80 (s, 1H, 8′-H), 6.85 (s, 1H, 5-H), 10.30 (*s*, 1H, 9-H)
26	200	$CDCl_3$	2.51 (*s*, 3H, 8-Me), 3.48 (*s*, 3H, 8′-OMe), 3.62 (*s*, 3H, 9′-OMe), 4.73 (*s*, 2H, 9′-CH_2–), 6.43 (*s*, 1H, 8′-H), 6.75 (*s*, 1H, 5-H), 8.35 [*s* (*br*), 1H, –OH], 10.42 (*s*, 1H, 9-H), 12.11 (*s*, 1H, –OH)
27	200	$CDCl_3$	1.23, 1.25 (2 × *t*, J = 7 Hz, 2 × 3H, 2 × –CH_2–Me), 2.52 (*s*, 3H, 8-Me), 3.67 (*q*, J = 7 Hz, 2H, 9′-O–CH_2–Me), 3.90 (*m*, 2H, 8′-O–CH_2–Me), 4.79 (*q*, J = 12 Hz, 9′-CH_2–), 6.50 (1H, *s*, 8′-H), 6.75 (1H, *s*, 5-H), 8.50 [*s* (*br*), 1H, –OH], 10.47 (*s*, 1H, 9-H), 12.14 (*s*, 1H, –OH)
	200	DMSO-d_6	1.10, 1.12 (2 × *t*, J = 7 Hz, 2 × 3H, 2 × –CH_2–Me), 2.43 (*s*, 3H, 8-Me), 3.33 (*s*, –OH), 3.52 (*q*, J = 7 Hz, 2H, 9′, -O–CH_2–Me), 3.70 (*m*, 2H, 8′-O–CH_2–Me), 4.58 (*s*, 2H, 9′-CH_2–), 6.81 (*s*, 1H, 8′-H), 6.89 (*s*, 1H, 5-H), 10.45 (*s*, 1H, 9-H).
28	200	DMSO-d_6	1.07 (*t*, J = 7 Hz, 3H, 8′-O–CH_2–Me), 2.49 (*s*, 3H, 8-Me), 3.35 [*s* (*br*), –OH], 3.67 (*m*, 2H, 8′-O–CH_2–Me), 4.66 (*s*, 2H, 9′-CH_2–), 6.81 (*s*, 1H, 8′-H), 6.89 (*s*, 1H, 5-H), 10.45 (*s*, 1H, 9-H)
29	200	DMSO-d_6	1.09 (*t*, J = 7 Hz, 3H, 9′-O–CH_2–Me), 2.42 (*s*, 3H, 8-Me), 3.34 (*s*, –OH), 3.48 (*q*, J = 7 Hz, 3H, 9′-O–CH_2–Me), 4.58 (*s*, 2H, 9′-CH_2–), 6.81 (*s*, 1H, 8′-H), 6.89 (*s*, 1H, 5-H), 8.30 (*s*, 1H, –OH), 10.45 (*s*, 1H 9-H)
30	200	$CDCl_3$	1.17, 1.23 (2 × *t*, J = 7 Hz, 2 × 3H, 2 × –CH_2–Me), 2.39, 2.43 (2 × *s*, 2 × 3H, 2 × –OAc), 2.56 (*s*, 3H, 8-Me), 3.55 (*q*, J = 7 Hz, 2H, 9′-O–CH_2–Me), 3.91 (*m*, 2H, 8′-O–CH_2–Me), 4.62 (*s*, 2H, 9′–CH_2–), 6.39 (*s*, 1H, 8′-H), 6.96 (*s*, 1H, 5-H), 10.54 (*s*, 1H, 9-H)
32	200	$CDCl_3$	1.39 [*s*, 9H, 9′-O–C(Me)$_3$], 2.43 (*s*, 3H, 8-Me), 4.80 (*s*, 2H, 9′-CH_2–), 5.90 (*s*, 1H, –OH), 6.57 (*s*, 1H, 8′-H), 6.59 (*s*, 1H, 5-H), 10.51 (*s*, 1H, 9-H), 12.15 (*s*, 1H, –OH)
Pentaacetylnorstictic acid			
	200	$CDCl_3$	2.07, 2.11, 2.21 (3 × *s*, 3 × 3H, 3 × –OAc), 2.30 (*s*, 3H, 9′-Me), 2.36, 2.44 (2 × *s*, 2 × 3H, 2 × –OAc), 2.52 (*s*, 3H, 8-Me), 6.95 (*s*, 1H, 5-H), 7.85 (*s*, 1H, 8′-H), 7.97 (*s*, 1H, 9-H)

silver oxide in acetone yielded 2',8'-di-*O*-methylstictic acid (**6**) in agreement with the work of Curd and Robertson [4]. Methylation of norstictic acid with dimethyl sulphate and potassium carbonate in dimethylformamide gave 2'-*O*-methylstictic acid (**7**).

Acetylation of the 8'-OH group, as shown in the case of pentaacetylnorstictic acid, shifted the signal of the 8'-proton in the NMR spectrum to 7.85 ppm (Table 2). The ^{1}H NMR spectrum of **4** does not show a signal in this region, which proved that methylation had occurred at the 8'-OH group.

Heating stictic acid with ethanol gave 8'-*O*-ethylstictic acid (**8**) which was acetylated by acetic anhydride/pyridine to 2'-*O*-acetyl-8'-*O*-ethylstictic acid (**9**) and by acetic anhydride/sulphuric acid to 9,9,2'-tri-*O*-acetyl-8'-*O*-ethylstictic acid (**10**). Methylation of **8** with dimethyl sulphate/potassium carbonate in dimethylformamide gave 2'-*O*-methyl-8'-*O*-ethylstictic acid (**11**).



Recently Ingolfsdottir *et al.* [5] reported the isolation of the new depsidone vesuvianic acid from *Stereocaulon vesuvianum* Pers. var. *pulvinatum* (Schaer.) Duncane and *S. alpinum* Laur. and put forward the structure **12** for this lichen substance. Comparison of the physical and spectroscopic data (Table 3) of **8** and **12** revealed the coidentity of these compounds; hence the structure of vesuvianic acid has to be corrected to **8**. Methyl- and ethylstictic acids reacted with aniline to give the corresponding anilides **13** and **14**, respectively.

Next we investigated the reaction of norstictic acid (**15**) with methanol and ethanol. Boiling **15** with methanol yielded 8'-*O*-methylnorstictic acid (**16**) which was acetylated with acetic anhydride/pyridine to 4,2'-*O*-acetyl-8'-*O*-methylnorstictic acid (**17**) and with acetic anhydride/sulphuric acid to 4,9,9,2'-tetra-*O*-acetyl-8'-*O*-methylnorstictic acid (**18**). From the mother liquor of **15**, after saturation with hydrochloric acid, the diphenylether **19** was isolated; it gave a red colour with sodium hypochlorite, proving the presence of two free, *meta* hydroxyl groups. On acetylation with acetic anhydride/pyridine **19** gave the triacetate **20**. Prolonged reaction of diazomethane on norstictic acid gave the diphenylether **21**. The ^{1}H NMR spectrum of **21** showed a signal at δ2.54 which corresponded to the additional methyl group at C-8'.

Heating norstictic acid with ethanol yielded 8'-*O*-ethylnorstictic acid (**22**) which was acetylated with acetic anhydride/pyridine to 4,2'-di-*O*-acetyl-8'-*O*-ethylnorstictic acid (**23**) and with acetic anhydride/sulphuric acid to 4,9,9,2'-tetra-*O*-acetyl-8'-*O*-ethylnorstictic acid (**24**).

Finally we looked for the reaction of methanol, ethanol and tert-butanol with salazinic acid (**25**). Boiling **25** with methanol gave 8',9'-di-*O*-methylsalazinic acid (**26**), while boiling with ethanol yielded 8',9'-di-*O*-ethylsalazinic acid (**27**), 8'-*O*-ethylsalazinic acid (**28**) and 9'-*O*-ethylsalazinic acid (**29**). Acetylation of **27** with acetic anhydride/pyridine gave 4,2'-di-*O*-acetyl-8',9'-di-*O*-ethylsalazinic acid (**30**).

In 1984 Handong *et al.* [6] described the isolation of a new depsidone, cetrariastrumin, from *Cetrariastrum nepalensis* Awasthi and put forward structure **31** for this lichen substance. Comparison of the physical and spectroscopic data (Table 3) showed the identity of cetrariastrumin with 8',9'-di-*O*-ethylsalazinic acid, a result found simultaneously by J. A. Elix*; hence the structure of cetrariastrumin has to be corrected to **27**.

Boiling of salazinic acid with *t*-butanol gave 9'-*O*-t-butylsalazinic acid (**32**).

*Letter from Dr. J. A. Elix to S.H. 1985.

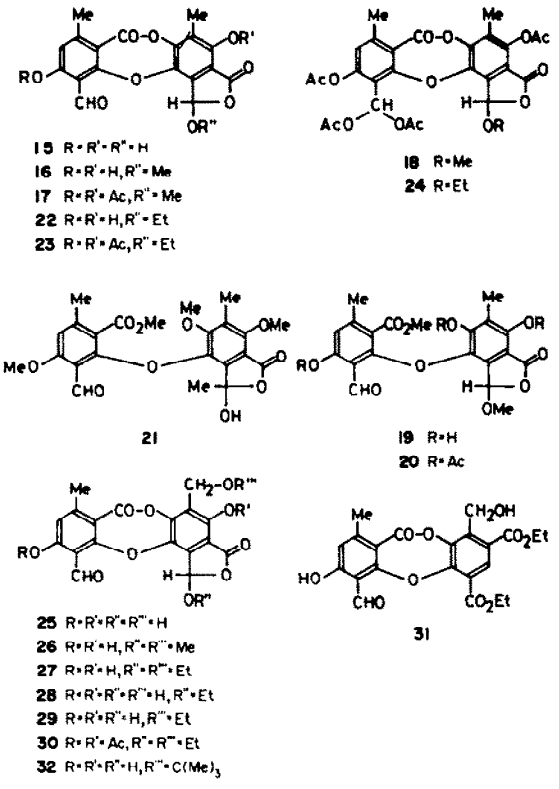
Table 3. Comparison of the physical and spectroscopic data of vesuvianic acid with those of 8'-*O*-ethylstictic acid

	Vesuvianic acid of Ingolfsdottir *et al.* [5]	8'-*O*-Ethylstictic acid
Mp	245°	245–246°
^{1}H NMR	1.29 (*t*, 3H), 2.30 (*s*, 3H), 2.57 (*s*, 3H), 3.98 (*s*, 3H), 4.01 (*q*, 2H), 6.49 (*s*, 1H), 6.75 (*s*, 1H), 7.92 (*s*, 1H), 10.54 (*s*, 1H) ($CDCl_3$)	1.35 (*t*, 3H), 2.40 (*s*, 3H), 2.70 (*s*, 3H), 3.96 (*m*, 2H), 4.16 (*s*, 3H), 6.70 (*s*, 1H), 7.24 (*s*, 1H), 10.24 (*s*, 1H), 10.60 (*s*, 1H) (200 MHz, DMSO-d_6)
MS, *m/z*	414, 370, 369, 368, 341, 340, 312, 287, 285, 210, 191, 58, 43	414, 385, 368, 358, 341, 340, 325, 312, 285, 268, 259, 256, 230, 221, 193, 191, 148

Remarkably we could not find the corresponding 9-dimethylacetals on reaction of norstictic and salazinic acids with methanol or ethanol. Probably the aldehyde group in both compounds is not so reactive because of the hydrogen bond between the 4-OH group and the aldehyde group.

The signals of the 8′-*O*-methylene protons in the ^{1}H NMR spectra of the compounds **8–11**, **22–24** and **27–30** appear as multiplets. The reason for this is the influence of the chiral centre at C-8′: both protons of the $-CH_2$ group in all conformations are always in different chemical surroundings relative to the proton at C-8′. In contrast to this the protons of the 9′-O–CH_2 group give a clear quartet and hence both groups can be easily distinguished. The splitting of the signal of the C-9′ benzylic group is noteworthy and means that free rotation along the C-3′–C-9′ axis is restricted; possibly the OH-group at C-2′ forms a hydrogen bond with the ether oxygen.

The results of our experiments demonstrate that depsidones with a lactole ring react with hot alcohols and consequently extraction of lichens with alcohols or solvents contaminated with alcohols (e.g. $CHCl_3$) should be avoided.



15 R = R′ = R″ = H
16 R = R′ = H, R″ = Me
17 R = R′ = Ac, R″ = Me
22 R = R′ = H, R″ = Et
23 R = R′ = Ac, R″ = Et

18 R = Me
24 R = Et

21

19 R = H
20 R = Ac

25 R = R′ = R″ = R‴ = H
26 R = R′ = H, R″ = R‴ = Me
27 R = R′ = H, R″ = R‴ = Et
28 R = R′ = R″ = H, R‴ = Et
29 R = R′ = R″ = H, R‴ = Et
30 R = R′ = Ac, R″ = R‴ = Et
32 R = R′ = R″ = H, R‴ = C(Me)$_3$

31

EXPERIMENTAL

8′-O-*Methylstictic acid* (2). Stictic acid (1.5 g) was heated under reflux with MeOH (600 ml) for 1 hr. After removal of the solvent *in vacuo*, the residue was adsorbed onto silica gel (3 g, with 0.5 M oxalic acid) which was then put on the top of a column of silica gel (60 g, with 0.5 M oxalic acid) in C_6H_6. Elution of the column with C_6H_6–Me_2CO (24:1) (500 ml) gave 8′-*O*-methylstictic acid (0.0786 g) as needles, mp 248–249° (from Me_2CO); $C_{20}H_{16}O_9$ (*m/z* 400.33). UV λ_{max}^{MeOH} nm (log ε): 218 (4.83), sh 260 (4.30), sh 310 (3.90); IR ν_{max}^{KBr} cm^{-1}: 710, 738, 762, 798, 870, 890, 936, 970, 982, 1030, 1095, 1140, 1160, 1218, 1266, 1300, 1350, 1388, 1450, 1498, 1558, 1606, 1694, 1738, 3000, 3500; MS *m/z* (rel. int.): 400 [M]$^+$ (100), 368 [M – MeOH]$^+$ (76), 355 (30), 340 (35), 325 (9), 312 (29), 297 (10), 285 (20), 270 (10), 259 (13), 193 (31), 191 (42), 164 (6), 148 (9). React.: K yellow, Cl yellow-orange. R_f 0.40 (silica gel, toluene–Et_2O–AcOH, 3:6:1, PD).

Stictic acid 9-dimethylacetal (3). Stictic acid (0.5 g) was heated under reflux with MeOH (500 ml) for 20 min, the solvent removed *in vacuo* and the residue fractionally recrystallized from $CHCl_3$–MeOH to give glistening prisms, mp 208–210° (dec.). $C_{21}H_{20}O_{10}$ (*m/z* 432.37). UV λ_{max}^{MeOH} nm (log ε): 214 (4.91), sh 264 (4.35), sh 309 (3.83); IR ν_{max}^{KBr} cm^{-1}: 710, 758, 790, 828, 870, 896, 934, 970, 988, 1016, 1074, 1100, 1142, 1160, 1190, 1228, 1266, 1294, 1374, 1450, 1494, 1562, 1606, 1730, 2980, 3500; MS *m/z* (rel. int.): 400 [M – MeOH]$^+$ (100), 385 (95), 368 (43), 356 (22), 341 (45), 312 (26), 284 (22), 259 (21), 193 (34), 191 (53), 166 (39), 165 (34), 148 (24), 134 (16), 120 (13), 106 (13). React.: K yellow, Cl yellow-orange.

2′-O-*Acetyl*-8′-O-*methylstictic acid* (4). Acetylation of 2

Table 4. Comparison of the physical and spectroscopic data of cetrariastrumin with those of 8′,9′-di-*O*-ethylsalazinic acid

	Cetrariastrumin [6]	8′,9′-Di-*O*-ethylsalazinic acid
Formula	$C_{22}H_{20}O_{10}$	$C_{22}H_{20}O_{10}$
Mp	163–165°	163–165°
UV, λ_{max} nm (log ε)	EtOH	MeOH
	216 (4.33), 239.5 (4.58), 306.5 (3.92), 355.5 (3.93)	212 (4.82), 237 (4.76), 310 (4.04)
IR ν_{max}^{KBr} cm^{-1}	1570, 1622, 1650, 1660, 1743, 1755, 1780, 3370	1570, 1620, 1655, 1755, 3450
^{1}H NMR ($CDCl_3$)	1.24 (3H, *t*, *J* = 7 Hz), 1.26 (3H, *t*, *J* = 7 Hz), 2.53 (3H,	1.23 (3H, *t*, *J* = 7 Hz), 1.25 (3H, *t*, *J* = 7 Hz), 2.52
δ (ppm)	*s*), 3.67 (2H, *q*, *J* = 7 Hz), 3.90 (2H, *q*, *J* = 7 Hz), 4.79	(3H, *s*), 3.67 (2H, *q*, *J* = 7 Hz), 3.91 (2H, *m*), 4.79 (2H,
	(2H, *s*), 6.51 (1H, *s*), 6.75 (1H, *s*), 8.60 (1H, *s*), 10.47	*dd*), 6.50 (1H, *s*), 6.75 (1H, *s*), 8.60 (1H, *s*), 10.47 (1H,
	(1H, *s*), 12.14 (1H, *s*) (90 MHz)	*s*), 12.14 (1H, *s*) (200 MHz)
^{13}C NMR ($CDCl_3$)	22.63 MHz	50.29 MHz
δ (ppm)	14.6, 15.2, 22.3, 62.2, 65.8, 67.0, 100.1, 109.2, 110.3,	14.7, 15.2, 22.2, 62.1, 65.9, 67.0, 100.3, 109.3, 110.5,
	118.2, 120.4, 135.0, 139.0, 149.9, 153.5, 153.9, 160.4,	111.9, 118.3, 120.7, 135.0, 138.8, 149.7, 153.7, 154.0,
	161.7, 165.2, 165.2, 167.0, 193.1	159.7, 164.4, 165.8, 167.8, 193.1
MS, *m/z*	444, 415, 399, 398, 369, 354, 341, 326, 314, 299, 286, 243,	444, 398, 369, 354, 341, 326, 314, 299, 285, 256, 185,
	215, 179, 177, 150, 134, 115, 106	179, 177, 150, 137, 115, 111

(0.1 g) with Ac_2O/C_5H_5N (1:1, 4 ml) at 20° for 24 hr and usual work up gave needles, mp 220–222° (from $CHCl_3$–MeOH). $C_{22}H_{18}O_{10}$ (442.36). IR ν_{max}^{KBr} cm^{-1}: 664, 724, 758, 784, 798, 820, 878, 914, 934, 970, 988, 1010, 1042, 1092, 1130, 1182, 1208, 1274, 1306, 1330, 1366, 1440, 1480, 1550, 1600, 1690, 1760, 2950; MS *m/z* (rel. int.): 442 $[M]^+$ (3), 428 (18), 410 $[M-MeOH]^+$ (33), 400 $[M-CH_2{=}C{=}O]^+$ (100), 386 (21), 368 (96), 355 (48), 340 (71), 324 (26), 312 (59), 285 (38), 284 (35), 259 (24), 231 (14), 193 (49), 191 (54), 165 (16), 148 (15).

9,9,2',8'-*Tetra*-O-*acetylstictic acid* (**5**). Treatment of **3** (0.1 g) with Ac_2O (3 ml) and H_2SO_4 (2 drops) at 20° in 24 hr, followed by usual work up and crystallization from $CHCl_3$–MeOH gave prisms mp 229–231°, identical with authentic tetraacetylstictic acid. $C_{28}H_{24}O_{15}$ (*m/z* 600.47). IR ν_{max}^{KBr} cm^{-1}: 696, 720, 750, 786, 810, 884, 920, 950, 966, 1000, 1050, 1090, 1140, 1190, 1270, 1310, 1370, 1444, 1482, 1562, 1608, 1760, 3000; MS *m/z* (rel. int.): 572 $[M-CO]^+$ (3), 530 $[M-CO-CH_2{=}C{=}O]^+$ (73), 502 (26), 470 (33), 442 (30), 428 (68), 411 (42), 400 (47), 386 (83), 368 (100), 340 (57), 312 (36), 285 (21), 259 (21), 254 (21), 217 (13), 193 (56), 166 (21), 142 (37), 127 (33).

2',8'-*Di*-O-*methylstictic acid* (**6**). **1** (1 g) was heated with MeI (10 ml) and Ag_2O (5 g) in Me_2CO (50 ml) under reflux for 2 hr. Usual work up and crystallization from EtOAc gave needles, mp 250–253°. $C_{21}H_{18}O_9$ (*m/z* 414.35). UV λ_{max}^{MeOH} nm (log ε): 215 (4.78), S 235 (4.68), S 270 (4.29); UV $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 215 (4.90), 245 (4.59), 319 (4.54); IR ν_{max}^{KBr} cm^{-1}: 660, 732, 760, 794, 818, 850, 880, 900, 926, 984, 1030, 1098, 1148, 1220, 1288, 1330, 1350, 1388, 1436, 1482, 1550, 1604, 1760, 3000; MS *m/z* (rel. int.): 414 $[M]^+$ (89), 399 $[M-Me]^+$ (22), 382 $[M-MeOH]^+$ (100), 355 (43), 354 (44), 353 (32), 339 (17), 327 (24), 326 (26), 325 (21), 311 (43), 297 (15), 222 (17), 194 (28), 191 (38), 165 (41), 142 (33).

2'-O-*Methylstictic acid* (**7**). Methylation of norstictic acid (0.32 g) in dimethylformamide (6 ml) with dimethyl sulphate (3 ml) and K_2CO_3 (2 g) at room temp. in 20 min, followed by usual work up and crystallization from Me_2CO gave needles, mp 295–298° (dec.). $C_{20}H_{16}O_9$ (*m/z* 400.33). IR ν_{max}^{KBr} cm^{-1}: 668, 750, 800, 826, 870, 900, 918, 970, 1024, 1090, 1100, 1150, 1228, 1290, 1358, 1390, 1430, 1486, 1550, 1606, 1690, 1740, 1764, 3000, 3470; MS *m/z* (rel. int.): 400 $[M]^+$ (72), 384 (26), 355 (50), 342 (38), 328 (26), 314 (35), 297 (28), 285 (27), 271 (20), 257 (25), 230 (20), 193 (100), 191 (56), 166 (44), 165 (40), 164 (42), 152 (34), 106 (29). React.: K yellow, Cl yellow.

8'-O-*Ethylstictic acid* (**8**). Stictic acid (2 g) was heated under reflux with EtOH (500 ml) for 26 hr. Removal of the solvent *in vacuo* and recrystallization of the residue from EtOH gave needles (1 g), mp 245–246° (dec.); $C_{21}H_{18}O_9$ (*m/z* 414.35); IR ν_{max}^{KBr} cm^{-1}: 760, 792, 810, 834, 864, 882, 934, 964, 1034, 1096, 1140, 1152, 1220, 1270, 1300, 1334, 1384, 1442, 1490, 1552, 1602, 1700, 1726, 2970, 3480; MS *m/z* (rel. int.): 414 $[M]^+$ (85), 385 $[M-CHO]^+$ (22), 368 $[M-EtOH]^+$ (100), 358 (18), 341 (56), 340 $[M-EtOH-CO]^+$ (59), 325 (24), 312 (57), 285 (51), 268 (22), 259 (35), 256 (27), 230 (18), 221 (13), 193 (72), 191 (71), 148 (33). React.: K yellow, Cl yellow-orange. R_f 0.72 (silica gel, toluene–Et_2O–AcOH, 3:6:1, PD).

2'-O-*Acetyl*-8'-O-*ethylstictic acid* (**9**). Acetylation of **8** (0.2 g) with Ac_2O–C_5H_5N (1:1, 4 ml) at 20° for 48 hr, followed by usual work up and crystallization from $CHCl_3$–MeOH gave needles, mp 170–172°. $C_{23}H_{20}O_{10}$ (*m/z* 456.39). IR ν_{max}^{KBr} cm^{-1}: 726, 760, 906, 938, 964, 990, 1020, 1050, 1124, 1140, 1182, 1208, 1274, 1306, 1364, 1400, 1440, 1482, 1554, 1602, 1690, 1764, 2980; MS *m/z* (rel. int.): 456 $[M]^+$ (45), 414 $[M-CH_2{=}C{=}O]^+$ (100), 398 (36), 384 (33), 368 $[M-CH_2{=}C{=}O-EtOH]^+$ (97), 340 (64), 312 (50), 285 (36), 259 (24), 193 (54), 191 (67), 177 (21), 164 (23), 148 (18), 142 (24), 127 (15). React.: K yellowish, Cl yellowish.

9,9,2'-*Tri*-O-*acetyl*-8'-O-*ethylstictic acid* (**10**). Acetylation of **8** with Ac_2O (3 ml) and H_2SO_4 (1 drop) at 20° for 48 hr gave, after usual work up and crystallization from $CHCl_3$–MeOH, prisms, mp 125–128°. $C_{27}H_{36}O_{13}$ (*m/z* 558.48); IR ν_{max}^{KBr} cm^{-1}: 746, 768, 780, 904, 940, 970, 1018, 1094, 1150, 1200, 1230, 1272, 1312, 1368, 1448, 1480, 1556, 1610, 1764, 3020; MS *m/z* (rel. int.): 516 $[M-CH_2{=}C{=}O]^+$ (52), 456 $[M-CH_2{=}C{=}O-AcOH]^+$ (51), 414 $[M-2CH_2{=}C{=}O-AcOH]^+$ (100), 368 $[M-2CH_2{=}C{=}O-AcOH-EtOH]^+$ (98), 340 (35), 312 (23), 285 (17), 259 (10), 227 (7), 193 (36), 191 (26), 177 (10), 142 (17), 127 (10).

2'-O-*Methyl*-8'-O-*ethylstictic acid* (**11**). Methylation of **8** (0.5 g) with dimethyl sulphate (2 ml) and K_2CO_3 (1.5 g) in dimethylformamide (2 ml), followed by usual work up and crystallization from $CHCl_3$–MeOH gave needles, mp 207–209°. $C_{22}H_{20}O_9$ (*m/z* 428.38); IR ν_{max}^{KBr} cm^{-1}: 760, 790, 810, 872, 900, 960, 1000, 1024, 1100, 1130, 1180, 1214, 1290, 1336, 1354, 1378, 1402, 1426, 1480, 1550, 1602, 1692, 1728, 1744, 2960; MS *m/z* (rel. int.): 428 $[M]^+$ (86), 414 (35), 382 $[M-EtOH]^+$ (100), 368 (40), 355 (70), 341 (35), 327 (46), 311 (49), 285 (27), 259 (27), 226 (26), 208 (49), 193 (97), 191 (81), 179 (59), 165 (81), 151 (40), 135 (16). ^{13}C NMR (50.29 MHz, $CDCl_3$): 114.9 (C-1), 162.9 (C-2), 115.3 (C-3), 163.9 (C-4), 112.2 (C-5), 151.7 (C-6), 165.3 (C-7), 22.34 (C-8), 186.81 (C-9), 99.4 (C-1') 155.6 (C-2') 127.6 (C-3'), 148.7 (C-4') 140.9 (C-5') 135.5 (C-6') 160.6 (C-7'), 112.2 (C-8'), 10.04 (C-9'), 15.01 (-O-CH_2-$\underline{C}H_3$), 65.99 (-O-$\underline{C}H_2$-CH_3), 56.76 and 62.74 (OMe). React.: K –, Cl –.

Anilide of 8'-O-*methylstictic acid* (**13**). To a boiling soln of **3** (50 mg) in EtOH (6 ml) was added freshly distilled aniline (2 drops). The heavily soluble precipitate was filtered and washed with EtOH. Colourless prisms mp 208–210°. $C_{26}H_{21}NO_8$ (*m/z* 475.43). IR ν_{max}^{KBr} cm^{-1}: 700, 782, 806, 840, 864, 894, 908, 948, 990, 1058, 1080, 1116, 1148, 1190, 1226, 1270, 1298, 1326, 1352, 1380, 1460, 1510, 1530, 1560, 1610, 1640, 1728, 3000, 3500; MS *m/z* (rel. int.): 475 $[M]^+$ (70), 460 (23), 400 (58), 385 (35), 368 (35), 340 (41), 284 (29), 191 (65), 166 (41), 165 (35), 164 (29), 143 (23), 119 (100).

Anilide of 8'-O-*ethylstictic acid* (**14**). A soln of **8** (20 mg) in EtOH (6 ml) was boiled with aniline (2 drops) for 3 min, the soln concentrated to a vol. of 1.5 ml, and the precipitate which formed filtered and washed with EtOH: yellowish needles, mp 203–205°. $C_{27}H_{23}NO_8$ (*m/z* 489.45). MS *m/z* (rel. int.): 489 $[M]^+$ (48), 460 (100), 445 (21), 432 (11), 416 (14), 397 (14), 389 (11), 351 (43), 323 (12), 295 (16), 268 (16), 241 (21), 194 (7), 159 (18), 107 (18).

8'-O-*Methylnorstictic acid* (**16**). Norstictic acid (0.1 g) was heated with MeOH (100 ml) under reflux for 28 hr. After removal of the solvent *in vacuo*, crystallization of the residue (Me_2CO–H_2O) gave silk-like needles, mp 300–302° (dec.). $C_{19}H_{14}O_9$ (*m/z* 386.30); IR ν_{max}^{KBr} cm^{-1}: 784, 800, 854, 898, 930, 962, 970, 1022, 1088, 1144, 1160, 1300, 1380, 1450, 1490, 1560, 1620, 1652, 1740, 2950, 3440. React.: K yellow, Cl yellow-orange. R_f 0.82 (silica gel, toluene–Et_2O–AcOH, 3:6:1, PD).

4,2'-O-*Acetyl*-8'-O-*methylnorstictic acid* (**17**). Acetylation of **16** (0.1 g) with Ac_2O–C_5H_5N (1:1, 2 ml) at 20° for 24 hr, followed by usual work up and crystallization ($CHCl_3$–MeOH) gave needles mp 247–249°. $C_{23}H_{18}O_{11}$ (*m/z* 470.37); IR ν_{max}^{KBr} cm^{-1}: 740, 756, 790, 826, 848, 920, 938, 978, 1026, 1076, 1144, 1190, 1252, 1278, 1310, 1372, 1390, 1440, 1482, 1560, 1608, 1690, 1770, 2970; MS *m/z* (rel. int.): 428 $[M-CH_2{=}C{=}O]^+$ (100), 396 $[M-CH_2C{=}O-MeOH]^+$ (18), 385 $[M-CH_2{=}C{=}O-CH_3-CO]^+$ (60), 354 $[M-2CH_2{=}C{=}O-MeOH]^+$ (88), 341 (44), 330 (16), 326 (40), 310 (6), 298 (31), 282 (7), 270 (9), 242 (5), 179 (10), 177 (9), 148 (8).

4,9,9,2'-*Tetra*-O-*acetyl*-8'-O-*methylnorstictic acid* (**18**). Acetylation of **16** (0.05 g) with Ac_2O (2 ml) and H_2SO_4 (1 drop) at 20° for 24 hr, followed by usual work up and crystallization ($CHCl_3$–MeOH) gave prisms, mp 203–204°. $C_{27}H_{24}O_{14}$ (*m/z* 572.46); IR ν_{max}^{KBr} cm^{-1}: 750, 914, 940, 1010, 1058, 1094, 1130, 1198, 1240, 1274, 1300, 1374, 1442, 1486, 1570, 1610, 1760, 3000; MS *m/z* (rel. int.): 530 $[M-MeOH]^+$ (93), 470 $[M-MeOH$

$-AcOH]^+$ (46), 456 (13), 439 (21), 428 [M − MeOH − AcOH $-CH_2$=C=O]$^+$ (100), 396 (22), 386 (66), 372 (14), 353 (98), 341 (40), 326 (34), 310 (11), 298 (30), 282 (8), 270 (10), 254 (6), 221 (8), 179 (17), 177 (10), 148 (9).

Diphenylether **19**. Norstictic acid (1 g) was heated under reflux with MeOH (800 ml) for 16 hr, the soln concentrated to a vol. of 200 ml and the precipitate (**16**) removed after 12 hr at 20°. The mother liquor was saturated with HCl at 0° and kept at this temp. for 3 hr. Then the solvent was removed *in vacuo*, the residue treated with Me_2CO (10 ml), the insoluble fraction filtered and recrystallized twice (Me_2CO) to give rectangular prisms mp 203–205°. $C_{20}H_{18}O_{10}$ (*m/z* 418.34); UV λ_{max}^{MeOH} nm (log ε): 230 (4.54), 263 (4.27), 313 (3.80); UV $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 207 (4.59), 247 (4.48), 327 (4.08); IR ν_{max}^{KBr} cm^{-1}: 670, 706, 756, 782, 794, 810, 872, 890, 918, 964, 992, 1022, 1100, 1172, 1200, 1292, 1340, 1390, 1458, 1502, 1576, 1650, 1720, 1742, 2960, 3500; MS *m/z* (rel. int.): 418 $[M]^+$ (68), 386 $[M-MeOH]^+$ (82), 354 $[M-2MeOH]^+$ (39), 341 (29), 327 (41), 299 (23), 270 (10), 245 (5), 208 (68), 194 (12), 179 (100), 177 (64), 163 (15), 150 (20), 122 (6). React.: K yellow, Cl red.

Triacetate of diphenylether **19** (**20**). Acetylation of **19** (50 mg) with Ac_2O–C_5H_5N (1:1, 2 ml) at 20° for 24 hr, followed by usual work up and crystallization (MeOH–H_2O) gave prisms, mp 131–133°. $C_{26}H_{24}O_{13}$ (*m/z* 544.45); IR ν_{max}^{KBr} cm^{-1}: 736, 802, 910, 930, 974, 1020, 1056, 1092, 1152, 1180, 1280, 1340, 1380, 1390, 1448, 1474, 1570, 1610, 1646, 1692, 1730, 1774, 3000; MS *m/z* (rel. int.): 502 $[M-CH_2=C=O]^+$ (63), 460 $[M-2CH_2=C=O]^+$ (100), 428 $[M-2CH_2=C=O-MeOH]^+$ (48), 418 $[M-3CH_2=C=O]^+$ (16), 400 (33), 386 (46), 369 (13), 358 (51), 354 (49), 341 (24), 327 (26), 299 (15), 251 (73), 221 (18), 208 (87), 194 (16), 179 (68), 150 (11).

Diphenylether **21**. To a soln of norstictic acid (0.2 g) in Me_2CO (200 ml) was added an ethereal soln of CH_2N_2, the mixture kept at 20° for 3 hr and the excess of CH_2N_2 destroyed by a few drops of HOAc. The solvent was removed *in vacuo*, the residue treated with MeOH (3 ml), and the precipitate filtered and crystallized (×2) from $CHCl_3$–MeOH to give needles, mp 182–184°. $C_{23}H_{24}O_{10}$ (*m/z* 460.43); IR ν_{max}^{KBr} cm^{-1}: 810, 866, 928, 1000, 1040, 1136, 1202, 1284, 1336, 1386, 1460, 1564, 1606, 1730, 2980, 3500; MS *m/z* (rel. int.): 442 $[M-H_2O]^+$ (74), 427 (68), 339 (26), 383 (100), 371 (19), 368 (17), 354 (24), 339 (23), 325 (8), 311 (24), 177 (16).

8′-O-*Ethylnorstictic acid* (**22**). Norstictic acid (0.8 g) was heated under reflux with EtOH (750 ml) for 22 hr and then the soln concentrated to a vol. of 400 ml. The crystals which separated after cooling were removed by filtration and recrystallized first from EtOH and then from Me_2CO to give needles (0.2 g), mp 240–242°, $C_{20}H_{16}O_9$ (*m/z* 400.33); IR ν_{max}^{KBr} cm^{-1}: 680, 802, 860, 962, 1028, 1038, 1100, 1164, 1208, 1258, 1300, 1350, 1390, 1456, 1500, 1578, 1660, 1754, 3000, 3510; MS *m/z* (rel. int.): 400 $[M]^+$ (100), 355 (75), 354 $[M-EtOH]^+$ (87), 344 (18), 327 (58), 326 (54), 298 (56), 271 (35), 270 (37), 245 (33), 242 (28), 216 (13), 179 (46), 177 (33), 176 (35), 148 (59). React.: K yellow, Cl yellow-orange. R_f 0.92 (silica gel, toluene–Et_2O–AcOH, 3:6:1, PD).

4,2′-*Di*-O-*acetyl*-8′-O-*ethylnorstictic acid* (**23**). Acetylation of **22** (0.1 g) with Ac_2O–C_5H_5N (0.5:1, 1.5 ml) at 20° for 24 hr followed by usual work up gave prismatic needles, mp 200–202° (from $CHCl_3$–MeOH). $C_{24}H_{20}O_{11}$ (*m/z* 484.40); IR ν_{max}^{KBr} cm^{-1}: 734, 750, 788, 834, 870, 900, 934, 960, 1018, 1070, 1092, 1120, 1146, 1182, 1244, 1270, 1304, 1370, 1440, 1480, 1554, 1602, 1630, 1690, 1766, 2950.

4,9,9,2′-*Tetra*-O-*acetyl*-8′-O-*ethylnorstictic acid* (**24**). Acetylation of **22** (0.2 g) with Ac_2O (3 ml) and H_2SO_4 (1 drop) at 20° for 24 hr and usual work up gave prisms, mp 165–166° (from $CHCl_3$–MeOH). $C_{28}H_{26}O_{14}$ (*m/z* 586.49); IR ν_{max}^{KBr} cm^{-1}: 706, 744, 782, 804, 900, 910, 934, 962, 1012, 1090, 1124, 1190, 1236, 1270, 1300, 1370, 1438, 1480, 1564, 1604, 1760, 3000.

8′,9′-*Di*-O-*methylsalazinic acid* (**26**). Salazinic acid (1 g) was heated under reflux in MeOH (600 ml) for 20 hr and then the solvent removed *in vacuo*. The residue was adsorbed onto silica gel (1.5 g, with 0.5 M oxalic acid) and the gel put on the top of a column of silica gel (15 g, with 0.5 M oxalic acid) C_6H_6–Me_2CO (49:1, 250 ml) eluted the dimethyl ether. Needles (5 mg), mp 242–244° (dec., from $CHCl_3$–MeOH). $C_{20}H_{16}O_{10}$ (*m/z* 416.33); IR ν_{max}^{KBr} cm^{-1}: 802, 860, 902, 972, 1028, 1104, 1148, 1160, 1210, 1260, 1300, 1354, 1398, 1456, 1574, 1656, 1754, 2980, 3500; MS *m/z* (rel. int.): 416 $[M]^+$ (20), 384 $[M-MeOH]^+$ (84), 369 $[M-MeOH-Me]^+$ (100), 354 (13), 341 (13), 325 (30), 315 (12), 299 (16), 297 (13), 296 (15), 271 (10), 206 (12), 177 (53), 162 (25), 150 (16), 134 (33).

8′,9′-*Di*-O-*ethylsalazinic acid* (**27**), 8′-O-*ethylsalazinic acid* (**28**) *and* 9′-O-*ethylsalazinic acid* (**29**). Salazinic acid (1 g) was heated under reflux with EtOH (800 ml) for 26 hr, the solvent removed *in vacuo*, the residue adsorbed onto silica gel (2 g, with 0.5 M oxalic acid) and the gel put on the top of a column of silica gel (50 g, with 0.5 M oxalic acid). After C_6H_6 (750 ml), C_6H_6–Me_2CO (1:1, 500 ml) eluted the diethylether **27**. Needles (0.345 g), mp 164–165° (from $CHCl_3$–MeOH). $C_{22}H_{20}O_{10}$ (*m/z* 444.38); UV λ_{max}^{MeOH} nm (log ε): 212 (4.82), 237 (4.76), S 272 (4.27), 310 (4.04); UV $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 199 (4.91), 235 (4.72), 255 (4.74), 301 (4.44), 355 (4.31); IR ν_{max}^{KBr} cm^{-1}: 690, 810, 904, 966, 1028, 1040, 1100, 1142, 1162, 1208, 1258, 1296, 1342, 1360, 1392, 1456, 1572, 1654, 1754, 3040, 3560; MS *m/z* (rel. int.): 444 $[M]^+$ (20), 398 $[M-EtOH]^+$ (69), 369 $[M-EtOH-CHO]^+$ (84), 354 (24), 341 (17), 326 (30), 314 (10), 299 (14), 285 (20), 256 (21), 185 (27), 179 (21), 177 (44), 167 (38), 150 (45), 149 (100), 137 (38), 129 (62), 125 (56), 123 (51), 115 (38), 111 (83). ^{13}C NMR (50.29 MHz, $CDCl_3$): 109.3 (C-1), 164.4 (C-2), 111.9 (C-3), 165.8 (C-4), 118.3 (C-5), 153.6 (C-6), 167.8 (C-7), 22.2 (C-8), 193.1 (C-9), 100.3 (C-1′), 154.0 (C-2′), 120.7 (C-3′), 149.6 (C-4′), 138.7 (C-5′) 135.0 (C-6′), 159.7 (C-7′), 110.6 (C-8′), 62.1 (C-9′), 14.7 or 15.2 ($-O-CH_2-\underline{C}H_3$), 65.9 or 67.0 ($-O-\underline{C}H_2-CH_3$). R_f 0.81 (silica gel, toluene–Et_2O–AcOH, 3:6:1, PD).

Further elution of the column with C_6H_6–Me_2CO (24:1) gave a mixture of two compounds (R_f 0.52 and 0.45, silica gel PF 254 + 366, C_6H_6–dioxane–HOAc, 90:25:4, heating with 10% H_2SO_4 to 150°) which was separated by PTLC (0.1 g on 5 × 20 × 20 × 0.1 cm silica gel PF 254 + 366 plates, C_6H_6–dioxane–HOAc, 90:25:4). The upper band yielded 8′-*O*-ethylsalazinic acid (**28**) as needles, mp 202–204° (dec., from Me_2CO–H_2O). $C_{20}H_{16}O_{10}$ (*m/z* 416.33); UV λ_{max}^{MeOH} nm (log ε): 211 (4.80), 235 (4.61), S 272 (4.13), 310 (3.93); UV $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 210 (4.87), 250 (4.48), 303 (4.39); IR ν_{max}^{KBr} cm^{-1}: 690, 740, 806, 830, 864, 878, 906, 966, 1022, 1092, 1064, 1094, 1260, 1300, 1390, 1458, 1570, 1660, 1758, 3000, 3450; MS *m/z* (rel. int.): 416 $[M]^+$ (30), 370 $[M-EtOH]^+$ (100), 354 (20), 342 (35), 340 (45), 326 (35), 314 (45), 298 (40), 286 (35), 271 (25), 244 (30), 216 (25), 179 (65), 177 (50), 150 (75). The lower band gave 9′-*O*-ethylsalazinic acid (**29**) as needles mp 195–197° (dec., from Me_2CO–H_2O). $C_{20}H_{16}O_{10}$ (*m/z* 416.33); UV λ_{max}^{MeOH} nm (log ε): 213 (4.71), 237 (4.64), 310 (3.90); UV $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 209 (4.78), 233 (4.57), 254 (4.61), 303 (4.32), 350 (4.16); IR ν_{max}^{KBr} cm^{-1}: 800, 826, 862, 902, 930, 968, 1028, 1092, 1148, 1160, 1210, 1294, 1320, 1344, 1360, 1390, 1450, 1572, 1654, 1740, 1754, 3000, 3470, 3630; MS *m/z* (rel. int.): 400 (100), 369 (64), 354 (78), 327 (50), 326 (41), 298 (50), 271 (28), 270 (28), 245 (23), 216 (17), 196 (23), 179 (50), 177 (40), 152 (98), 151 (87), 150 (80), 148 (46), 122 (41), 106 (44).

4,2′-*Di*-O-*acetyl*-8′,9′-*di*-O-*ethylsalazinic acid* (**30**). Acetylation of **27** (0.1 g) with Ac_2O–C_5H_5N (1:1, 2 ml) at 20° for 24 hr, followed by usual work up and crystallization ($CHCl_3$–MeOH) gave needles, mp 186–188°. $C_{26}H_{24}O_{12}$ (*m/z* 528.45); IR ν_{max}^{KBr} cm^{-1}: 742, 762, 802, 816, 840, 908, 950, 964, 1026, 1110,

1140, 1180, 1250, 1276, 1340, 1380, 1448, 1486, 1564, 1610, 1692, 1770, 3000.

9'-O-t-Butylsalazinic acid (**32**). Salazinic acid (0.5 g) was heated under reflux with tert-butanol (400 ml) for 12 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (20 g) with 0.5 M oxalic acid). Elution of the column with C_6H_6–Me_2CO (24:1, 250 ml) gave the tert-butyl ether as prismatic plates (0.105 g) mp 167–169° (dec., from Me_2CO–Et_2O) $C_{27}H_{10}O_{10}$ (*m/z* 444.38); IR ν_{max}^{KBr} cm^{-1}: 700, 740, 788, 804, 890, 924, 960, 1018, 1098, 1162, 1200, 1258, 1298, 1376, 1394, 1456, 1576, 1654, 1740, 3040, 3450; MS *m/z* (rel. int.): 426 $[M-H_2O]^+$ (3), 382 (1), 370 (2), 248 (3), 222 (2), 205 (2), 179 (6), 151 (100), 150 (85), 134 (9), 123 (13), 106 (28).

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