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THE STRUCTURES OF RETIGERIC ACIDS A AND B FROM LICHENS OF THE *LOBARIA RETIGERA* GROUP

RUMIKO TAKAHASHI*, HSÜCH-CHING CHIANG†, NORIO AIMI‡, OSAMU TANAKA§ and SHOJI SHIBATA

Faculty of Pharmaceutical Sciences, University of Tokyo, Japan

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Abstract—Retigeric acids A and B were isolated from the lichens of the *Lobaria retigera* group and their structures were established to be Ia and VIa, respectively. The occurrence of these triterpenes in the lichens of the *Lobaria retigera* group, and in *L. kazawaensis* and *L. sachalinensis* is of chemotaxonomic interest.

INTRODUCTION

Lobaria is a genus of foliose lichens distributed in tropic and temperate zones, 83 of the 215 known species having been reported in East Asia. The generic subdivision of *Lobaria* is mainly based on the difference in phycobionts. Asahina[1] classifies Japanese *Lobaria* by the chemical constituents and by differences in algal symbionts as follows:
Section Lobarina: Gonidia—blue-green algae. *Lobaria retigera* group. *L. verrucosa* group.
Section Ricasolia: Gonidia—green algae. *Lobaria pulmonaria* group. *L. amplissima* group. *L. ercosa* group.

According to Yoshimura,[2] the difference in phycobionts is not a useful taxomic character, but the difference in the size of spores can be used to separate the sections, Lobaria (spores: fusiform) and Ricasolia (spores: acicular or linear at maturity). The lichens of the *Lobaria retigera* group contain 4 species which are distinguished by the presence or absence of isidia, as well as by a positive or negative colour reaction with *p*-phenylenediamine (PD):

Lobaria retigera group (Yoshimura's names[2] in brackets):

Isidiate	PD (−) *L. isidiosa* (Müll. Arg.) Vain (*L. retigera* (Bory) Trev).
	PD (+) *L. isidiosa* var. *subisidiosa* Asah. (L. isidiosa (Müll. Arg.) Vain).
Non-isidiate	PD (−) *L. retigera* (Bory) Trev. (*L. kurokawae* Yoshim.).
	PD (+) *L. subretigera* Inum., (*L. pseudopulmonaria* Gyeln.).

* Present address: Showa College of Pharmaceutical Sciences, Tsurumaki 5-1-8, Setagaya-ku, Tokyo.
† Present address: 1-121 Chung-Shang North Road, Taipei, Taiwan.
‡ Present address: Faculty of Pharmacy, Chiba University, Chiba.
§ Present address: Institute of Pharmaceutical Sciences, School of Medicine, Hiroshima University, Hiroshima.

[1] Y. ASAHINA, *J. Jap. Bot.* **9**, 269, 398 (1933).
[2] I. YOSHIMURA, *J. Hattori Bot. Lab.* No. 34, 231–264 (1971).

Nine phenolic compounds have been reported in *Lobaria* spp:[3,4] the depsides scrobiculin, gyrophoric acid, congyrophoric acid and tenuiorin; the depsidones stictic acid, norstictic acid and constictic acid; and usnic acid and thelephoric acid (a dark violet colouring matter in rhizines). Apart from these constituents, several triterpenoids, have been found in the lichens of the *Lobaria retigera* group and in *L. sachalinensis* Asah. and *L. kazawaensis* (Asah.) Yoshim. The structures are not known, except for retigeradiol[5a] which is presumably 3β,19β-dihydroxytaraxerane.

The present paper is concerned with the chemical structures of two triterpenoids retigeric acids A and B isolated from the above mentioned lichens of *L. retigera* group, especially from *L. isidiosa* (*L. retigera*), which was collected in the Eastern Himalayas, Bhutan, by one of the authors (T.) during the University of Tokyo botanical expedition of 1967.

RESULTS

As shown by TLC (Fig. 1), the lichens which contain triterpenoids as the main metabolites have less stictic and norstictic acids, while a metabolite compound L–A, m.p. 222°, occurs in the depsidone-rich lichens. With regard to the earlier work of Seshadri *et al.*, our retigeric acid A, m.p. 296–299°, is probably identical with their compound D, m.p. 289–291°, and our compound L–A, m.p. 222°, is presumably identical with their retigeranic acid (compound B), m.p. 218–221°.

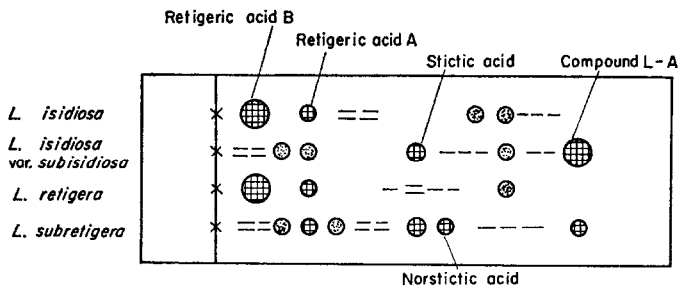


FIG. 1. TLC OF THE ETHEREAL EXTRACTS OF THE LICHENS OF THE *Lobaria retigera* GROUP. (Kiesel Gel GH Merck); Solvent: $CHCl_3$–MeOH–HCOOH (15:1:0·25).

Lichen material was extracted with ether and the precipitates formed on cooling were purified to obtain retigeric acid A. Retigeric acid B was isolated in the form of its methyl ester by the methylation of its mixture with retigeric acid A, followed by column chromatography.

Retigeric Acid A

Retigeric acid A (Ia), $C_{30}H_{48}O_4$, m.p. 296–299°, $[\alpha]_D$ +26·5° (c = 0·77 in pyridine) gave positive Liebermann–Burchard and tetranitromethane reactions. The IR spectrum indicated the presence of OH (3370 cm^{-1}) and C=O (1705 cm^{-1}). In the NMR spectrum, methyl retigerate A (Ib) showed 5 singlets of tertiary methyls (δ 0·72, 0·75, 0·81, 1·16, 1·24

[3] Y. ASAHINA and S. SHIBATA, *Chemistry of Lichen Substances*, Japan Society for Promotion of Science (1954).

[4] C. F. CULBERSON, *Chemical and Botanical Guide to Lichen Products*, University of North Carolina Press, Chapel Hill (1969); Suppl. to Chemical and Botanical Guide to Lichen Products. *Bryologist* **73**, 177 (1970).

[5](a) P. S. RAO and T. R. SESHADRI, *Indian J. Chem.* **6**, 1 (1968); (b) P. S. RAO, K. G. SARMA and T. R. SESHADRI, *Curr. Sci.* **34**, 9 (1965); *ibid.* **35**, 147 (1966).

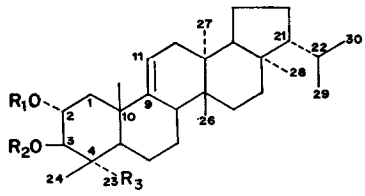
ppm), 2 doublets of methyls (δ 0·82 d. $J = 6$ Hz; 0·88 d. $J = 6$ Hz) in an isopropyl group, 1 singlet of methyl of $COOCH_3$ (δ 3·75), 1 proton signal of trisubstituted double bond (δ 5·38) and protons attached to the carbon atoms bearing OH [(δ 3·75) overlapped with the methyl ester signal]).

Retigeric acid A and its methyl ester (Ib) were acetylated to give diacetates, (IIa) and (IIb), respectively. On reduction with $LiAlH_4$ the methyl ester (Ib) yielded a triol (III) which afforded triacetate (IV). The NMR spectral signals of five tertiary methyls of retigeric acid A (Ia), its methyl ester (Ib) and their derivatives coincided with those given by the known fernanes[6] (Table 1). The MS of retigeric acid A and its derivatives gave similar fragmentation patterns with those of fern-9(11) ene and related compounds[7,8] (Table 2). This would suggest that retigeric acid A is a fernane derivative possessing a double bond at 9(11) and two hydroxyls and a carboxyl group on the ring A.

According to the coupling pattern ABXY [δ 5·08 (1H, sextet, $J_{AB} = 10$. $J_{AX} = 10$, $J_{AY} = 5$ Hz), 5·32 (1H, d. $J_{AB} = 10$ Hz)] of the protons at the carbons bearing OAc in methyl retigerate A diacetate (IIb), the secondary alcoholic hydroxyls in the A ring of retigeric acid A are present as a *trans* diequatorial glycol having an adjacent —CH_2— group. This can be located only at the 1,2 or 2,3 positions. The CH_2OAc signal of the triacetate of triol (III) appeared at δ 3·66 to give an equatorial conformation at the 4-position.[9]

Acetylation of methyl retigerate A (Ib) resulted in a down shift of the NMR signal of a methyl from δ 1·24 to 1·31 and another methyl signal from δ 1·16 to 1·22. Such a down field shift of methyl signal by the acetylation of hydroxyl has been observed in oleanane type triterpenes for 4β-Me and 3β-OH or 10β-Me and 2 α-OH.[10] In the IR spectrum of methyl retigerate A a partial hydrogen bonding between $COOCH_3$ and OH was observed.

All the above evidence leads to formula (Ia) for retigeric acid A. In order to confirm this structure, an X-ray crystallographical analysis of *p*-bromophenacyl retigerate A (V) was carried out by one of the present authors (T) and Prof. Y. Iitaka. The result of the X-ray analysis which supports the structural formula (Ia) will be reported elsewhere.



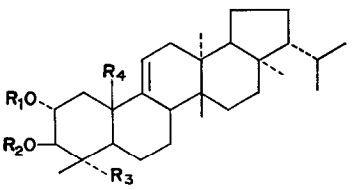
(Ia) $R_1 = R_2 = H$ $R_3 = COOH$
(Ib) $R_1 = R_2 = H$ $R_3 = COOCH_3$
(IIa) $R_1 = R_2 = Ac$ $R_3 = COOH$
(IIb) $R_1 = R_2 = Ac$ $R_3 = COOCH_3$
(III) $R_1 = R_2 = H$ $R_3 = CH_2OH$
(IV) $R_1 = R_2 = Ac$ $R_3 = CH_2OAc$
(V) $R_1 = R_2 = H$ $R_3 = COOCH_2CO$-C$_6$H$_4$-Br

Retigeric Acid B

Dimethyl retigerate B (VIb), $C_{32}H_{50}O_6$, was demethylated to give retigeric acid B (VIa) m.p. >268° (amorphous) and acetylated to give diacetate (VII), $C_{36}H_{54}O_8$, m.p. 180–181°, $[\alpha]_D$ −25° (c = 0·81 in $CHCl_3$). It was reduced with $LiAlH_4$ to yield the triol (VIII) and tetraol (X), which gave triacetate (IX) and tetraacetate (XI), respectively.

[6] H. AGETA, K. IWATA and S. NATORI, *Tetrahedron Letters* 1447 (1963).
[7] K. NISHIMOTO, M. ITO, S. NATORI and T. OHMOTO, *Tetrahedron* **24**, 735 (1968).
[8] H. BUDZIKIEWICZ, J. M. WILSON and C. DJERASSI, *J. Am. Chem. Soc.* **85**, 3688 (1963).
[9] A. GAUDEMER, J. POLONSKY and E. WENKERT, *Bull. Soc. Chim. Fr.* 407 (1964).
[10] S. ITO, M. KODAMA, M. SUNGAWA, T. OBA and H. HIKINO, Tetrahedron Letters 2905 (1969).

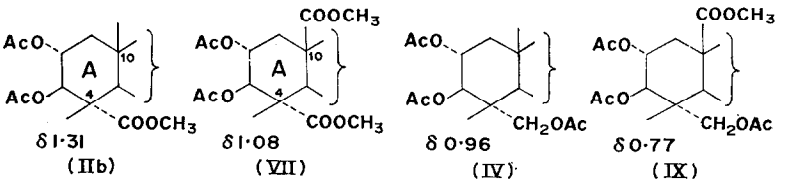
The NMR spectra of the derivatives of retigeric acid B revealed the presence of isopropyl groups and a double bonds in their structures. By analogy with retigeric acid A, retigeric acid B can be regarded as a fernane derivative having 2 OH and 2 COOH, and its structure can be formulated as (VIa).

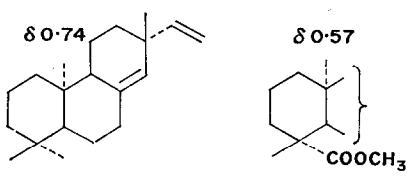


(VIa) $R_1 = R_2 = H$ $R_3 = R_4 = COOH$
(VIb) $R_1 = R_2 = H$ $R_3 = R_4 = COOCH_3$
(VII) $R_1 = R_2 = Ac$ $R_3 = R_4 = COOCH_3$
(VIII) $R_1 = R_2 = H$ $R_3 = CH_2OH$, $R_4 = COOCH_3$
(IX) $R_1 = R_2 = Ac$ $R_3 = CH_2OAc$, $R_4 = COOCH_3$
(X) $R_1 = R_2 = H$ $R_3 = R_4 = CH_2OH$
(XI) $R_1 = R_2 = Ac$ $R_3 = R_4 = CH_2OAc$

The presence of all the functional groups on ring A was proved by the retention of NMR signals of 5 of 6 methyls on changing these groupings (Table 1). The disposition of two hydroxyls at 2 and 3 positions, and one of the carboxyls at 4 position, similar to retigeric acid A, was proved by the following evidence: (1) tetraol acetate (XI) gave signals of CH_2-OAc at δ 3·47 (s), 4·14 and 4·33 (a pair of doublets 1H each, $J = 12$ Hz), which suggested the presence of one of the carboxyls of retigeric acid B at 4α corresponding to that of retigeric acid A. (2) The coupling pattern ABXY [δ 5·03 (1H, d, $J_{AB} = 10$ Hz), 5·27 (1H, sextet, $J_{AB} = 10, J_{AX} = 10, J_{AY} = 5$ Hz)] of the protons attached to the carbons bearing OAc of the compound (IX) was similar to that given by IIb, suggesting the same system of *trans* diequatorial glycol with adjacent methylene as in retigeric acid A. (3) The partial hydrogen bonding pattern of OH and $COOCH_3$ in the IR spectrum of dimethyl retigerate B resembles that given by methyl retigerate A (Ib). (4) One of the NMR signals of two $COOCH_3$ at δ 3·68 and 3·77, of dimethyl retigerate B is shifted by acetylation of hydroxyls upwards to give an overlapping signal at 3·68. Such an upward shift of NMR signal of $COOCH_3$ from 3·75 to 3·67 was observed on acetylation of methyl retigerate A. (5) On acetylation of methyl retigerate B, only one methyl signal is shifted from δ 0·98 to 1·08 as observed in methyl retigerate A to indicate the stereochemical correlation of 3β-OH and 4β-CH_3.

The position of another carboxyl of retigeric acid B at 10 position has been settled by the following evidence: (1) Comparison of the NMR spectra of methyl retigerate A diacetate





Methyl pimaradienate

(IIb) and triacetate (IV) of triol derived from retigeric acid A with those (VII and IX) of retigeric acid B shows that a methyl signal given by retigeric acid B derivatives appears further upfield (−0·23 and −0·19 ppm, respectively) than those of retigeric acid A. This would indicate a 1,3-diaxial disposition of $COOCH_3$ and CH_3 as revealed by methyl pimaradienate in comparison with pimaradiene.[11] This together with the stability of retigeric acid B to alkali, indicates that the carboxyl grouping must be located at 10β-position. (2) The NMR signals of the proton of trisubstituted double bond of dimethyl retigerate B (VIb) and its diacetate (VII) appear at a lower field (0·23 ppm) than those given by the corresponding derivatives of retigeric acid A. This suggests that one of the carboxyls of retigeric acid B is located close to the $\Delta^{9(11)}$ double bond. (3) The MS spectrum of dimethyl retigerate B showed *dd*, *ee* and *ff* peaks[8] as given by methyl retigerate A, but the former differs from the latter in giving an intense $M^+ - 59$ ($COOCH_3$) peak to reveal the presence of $COOCH_3$ grouping at an allylic position.

TABLE 1. THE NMR CHEMICAL SHIFTS (ppm FROM TMS) OF TRITERPENES AND THEIR DERIVATIVES

	CH_3							H	
	23	24	25	26	27	28	29 or 30		
X	0·85 or 0·88		1·04	0·72	0·80	0·75	0·82 (d)* 0·88 (d)	5·30	
Y	0·85 or 0·92		1·18	0·72	0·79	0·75	0·82 (d) 0·88 (d)	5·30	
Ib		1·24	1·16	0·72	0·81	0·75	0·82 (d) 0·88 (d)	5·40	3·75 ($COOCH_3$)
IIb		1·31	1·22	0·72	0·81	0·75	0·82 (d) 0·88 (d)	5·35	3·67 ($COOCH_3$)
IV		0·96	1·22	0·72	0·80	0·75	0·82 (d) 0·88 (d)	5·33	3·66 (CH_2OAc)
V		1·29	1·18	0·73	0·80	0·73	0·83 (d) 0·89 (d)	5·38	
VIb		0·98		0·69	0·83	0·77	0·84 (d) 0·90 (d)	5·63	3·77 ($COOCH_3$) 3·68 ($COOCH_3$)
VII		1·08		0·69	0·82	0·77	0·84 (d) 0·90 (d)	5·58	3·68 ($2COOCH_3$)
IX		0·77		0·68	0·82	0·75	0·83 (d) 0·89 (d)	5·57	3·68 (CH_2OAc) 3·68 ($COOCH_3$)
XI		0·98		0·69	0·81	0·76	0·82 (d) 0·88 (d)	5·44	3·70 (CH_2OAc) 4·14, 4·33 (a pair of doublets, 1H each, J = 12 Hz)

X = Fern-9(11)-ene. Y = Fernenediol diacetate.[12]
* Coupling constant J = 6 Hz.

Retigeric acids A and B are the first examples of migrated hopane type triterpenes occurring in lichens, and retigeric acid B is unusual among triterpenes in having an angular carboxyl at the $C_{(10)}$ position. Retigeric acids A and B occur in the lichens of the *Lobaria retigera* group as well as in *L. sachalinensis* and *L. kazawaensis* which belong to the *Lobaria pulmonaria* group. According to Yoshimura's new classification based on the shape of spores,[2] the latter two species are in the same section with the *Lobaria retigera* group though their phycobiont is different from *L. retigera*. Our present results provide support for Yoshimura's system.

[11] S. MIHASHI and O. TANAKA, *Tetrahedron Letters* 1683 (1969).
[12] H. WADA, G. GOTO, T. GOTO and Y. HIRATA, *Tetrahedron Letters* 3461 (1966).

TABLE 2. MASS SPECTRAL DATA

			Fernenediol diacetate		
			526	(79)	(M^+)
			511	(100)	(M^+-15)
			466	(11)	(M^+-60)
			451	(25)	(M^+-60-15)
			406	(82)	(M^+-2 × 60)
			391	(94)	(M^+-2 × 60-15)
			373	(8)	(*ff*)
			359	(84)	(*ee*)
			347	(8)	(*dd*)
			299	(13)	(*ee*-60)
			253	(32)	(*ff*-2 × 60)
			239	(88)	(*ee*-2 × 60)
			227	(29)	(*dd*-2 × 60)
			205	(36)	(*bb*)
Methyl retigerate A (Ib)			Methyl retigerate A diacetate (IIb)		
486	(38)	(M^+)	570	(13)	(M^+)
471	(100)	(M^+-15)	555	(23)	(M^+-15)
453	(21)	(M^+-15-18)	510	(13)	(M^+-60)
435	(11)	(M^+-15-2 × 18)	495	(6)	(M^+-60-15)
426	(8)	(M^+-60)	468	(4)	
411	(17)	(M^+-15-60)	450	(25)	(M^+-2 × 60)
393	(17)	(M^+-15-60-18)	435	(46)	(M^+-2 × 60-15)
375	(8)	(M^+-15-60-2 × 18)	417	(6)	(*ff*)
365	(9)		403	(55)	(*ee*)
333	(22)	(*ff*)	391	(15)	(*dd*)
319	(78)	(*ee*)	375	(15)	(M^+-3 × 60-15)
307	(23)	(*dd*)	343	(11)	(*ee*-60)
301	(23)	(*ee*-18)	324	(11)	
283	(17)	(*ee*-2 × 18)	309	(11)	
259	(16)		297	(19)	
241	(44)		283	(100)	(*ee*-2 × 60)
205	(21)	(*bb*)	271	(30)	
			205	(38)	(*bb*)
Dimethyl retigerate B (VIb)			(VIII)		
530	(40)	(M^+)	502	(49)	(M^+)
515	(76)	(M^+-15)	487	(61)	(M^+-15)
471	(79)	(M^+-59)	484	(10)	(M^+-18)
453	(100)	(M^+-59-18)	470	(9)	(M^+-32)
435	(40)	(M^+-59-2 × 18)	466	(6)	(M^+-2 × 18)
411	(26)	(M^+-59-60)	453	(49)	(M^+-59)
393	(40)	(M^+-59-60-18)	443	(27)	(M^+-15-3 × 18)
377	(20)	(*ff*)	425	(100)	(M^+-59-18)
375	(20)		407	(60)	(M^+-59-2 × 18)
363	(50)	(*ee*)	390	(12)	(M^+-59-3 × 18)
351	(17)	(*dd*)	380	(13)	
299	(20)		364	(7)	
275	(20)	(*ee*-18-60)	349	(8)	(*ff*)
267	(26)	(*ee*-2 × 18-60)	335	(31)	(*ee*)
255	(26)	(*dd*-2 × 18-60)	323	(10)	(*dd*)
231	(57)		317	(5)	(*ee*-18)
205	(76)	(*bb*)	303	(11)	(*ee*-32)
			291	(8)	
			273	(20)	
			271	(20)	
			257	(12)	(*ee*-18-60)
			239	(11)	(*ee*-2 × 18-60)
			205	(33)	(*bb*)

EXPERIMENTAL

M.ps were taken on a Kofler hot-stage apparatus and are uncorrected, and NMR spectra were determined on 100 Mc in $CDCl_3$.

Extraction of Lobaria isidiosa (Müll. Arg) Vain. (*L. retigera* (Bory) Trev. by Yoshimura). The lichen (dry wt 130 g) collected in Buhtan, the eastern Himalayas in 1967, was ground into fine powder and extracted (Soxhlet) with ether for 2 days. The precipitates (3·7 g) separated during extraction were chromatographed on a silica gel column (165 g), to elute retigeric acid A (0·16 g) with $CHCl_3$–MeOH (10:1). When the mixture of triterpene fraction was treated with CH_2N_2 followed by chromatography on a column, retigeric acid B was isolated in the form of its methyl ester (0·45 g).

Retigeric acid A (Ia) m.p. 296–299° (from EtOAc–MeOH–H_2O), colourless crystals, $[\alpha]_D$ +26·5 (c = 0·77 in pyridine) and ν_{max}^{KBr} 3370 (OH), 1705 (COOH) cm^{-1}. *Methyl retigerate A* (Ib) Treatment of Ia with CH_2N_2 gave Ib, m.p. 259–261° (from acetone), colourless crystals, $\nu_{max}^{CCl_4}$ 3615, 3580 (OH), 1740, 1725 ($COOCH_3$) cm^{-1} and δ 0·72, 0·75, 0·81, 1·16, 1·24 (1 Me each), 0·82 (d), 0·88 (d) (1Me each J = 6 Hz), 3·75 ($COOCH_3$), 3·3–3·9 (2H), 5·40 (1H, br) ppm. (Found: C, 76·74; H, 10·34. $C_{31}H_{50}O_4$ required: C, 76·50; H, 10·36%.) The *diacetate* (IIa) of retigeric acid A crystallized from MeOH–H_2O with m.p. 178–182°, colourless crystals, $\nu_{max}^{CCl_4}$ 1755, 1710 cm^{-1}. (Found: C, 73·05; H, 9·49. $C_{34}H_{52}O_6$ required: C, 73·34; H, 9·41 %.) Acetylation of methyl retigerate A gave a gelatinous solid from MeOH–H_2O, $\nu_{max}^{CCl_4}$ 1750, 1745 cm^{-1}, and δ 0·72, 0·75, 0·81, 1·22, 1·31 (1 Me each), 0·82 (d), 0·88 (d) (1 Me each, J = 6 Hz), 1·98 (2OAc), 3·67 ($COOCH_3$), 5·35 (1H, br), 5·32 (1H, d, J_{AB} = 10 Hz), 5·08 (1H, sextet, J_{AB} = 10, J_{AX} = 10, J_{AY} = 5 Hz).

$LiAlH_4$ *reduction of* Ib. Ib (0·2 g) in dry ether (60 ml) was refluxed with $LiAlH_4$ (0·1 g) for 4 hr. After working up, the product was crystallized from acetone to give triol (III), m.p. 255–258°, colourless crystals, $[\alpha]_D^{17}$ −22 (c = 0·53 in pyridine). ν_{max}^{KBr} 3590–3400 (OH), no carbonyl. (Found: C, 78·50; H, 10·91. $C_{30}H_{50}O_4$ required: C, 78·55; H, 10·99%). Acetylation of III gave triacetate IV (a single spot on TLC) δ 0·72, 0·75, 0·80, 0·96, 1·22 (1Me each), 0·82 (d), 0·88 (d) (1Me each, J = 6 Hz), 1·99, 2·02, 2·09 (1OAc each), 3·68 (s, CH_2OAc), 4·9–5·3 (2H), 5·33 (1H, br).

p-*Bromophenacyl ester* (V). After a solution of retigeric acid A (Ia) (*ca.* 0·09 g) in EtOH (10 ml) was neutralized with 1 N NaOH, a small amount of retigeric acid A (*ca.* 0·001 g) was added and the mixture refluxed with *p*-bromophenacyl bromide (0·06 g) in EtOH (3 ml) for 1 hr. The reagent (0·035 g) was added again and the reaction proceeded for another 1·5 hr when the reaction mixture was left overnight at room temp. The crude product was chromatographed on silica gel in $CHCl_3$. Crystallization from EtOAc–MeOH–H_2O gave V m.p. 245–247° $[\alpha]_D^{24·5}$ +12·3 (c = 0·46 in $CHCl_3$), ν_{max}^{KBr} 3550, 3460, 1725, 1690, 1590, 1220, 817 cm^{-1} and δ 0·73 (2Me), 0·80, 1·18, 1·29 (1 Me each), 0·83 (d), 0·89 (d) (1Me each, J = 6 Hz), 3·6–4·2 (2H), 5·28, 5·54 (a pair of doublets, 1H each, J = 17 Hz), 5·40 (1H, br). 7·63, 7·78 (a pair of doublets, 2H each, J = 11 Hz) ppm.

Dimethyl retigerate B (VIb). VIb purified by chromatography gave a positive Liebermann–Burchard reaction (yellowish orange) and tetranitromethane reaction, $\nu_{max}^{CCl_4}$ 3625, 3600 (OH), 1775, 1730 ($COOCH_3$) cm^{-1}, and δ 0·69, 0·77, 0·83, 0·98 (1Me each), 0·84 (d), 0·90 (d) (1Me each, J = 6 Hz), 3·68, 3·77 (1 $COOCH_3$ each), 3·6–3·9 (2H), 5·63 (1H, br). Demethylation with 5% methanolic KOH and repeated crystallization of the product from MeOH–H_2O gave an amorphous precipitate of retigeric acid B (VIa), m.p. >268°, positive Liebermann–Burchard reaction and tetranitromethane reaction and ν_{max}^{KBr} 3440, 1720, 1685 cm^{-1}. Acetylation of VIb gave VII, m.p. 180–181° (from MeOH–H_2O), colourless crystals, $[\alpha]_D$ −31·0° (c = 0·81 in $CHCl_3$), $\nu_{max}^{CCl_4}$ 1755, 1740 (sh), 1230 cm^{-1}, and δ 0·69, 0·77, 0·82, 1·08 (1Me each), 0·84 (d), 0·90 (d) (1Me each, J = 6Hz), 1·97, 2·00 (1OAc each), 3·68 (2 $COOCH_3$), 5·0–5·5 (2H), 5·58 (1H ,br). (Found: C, 70·32; H, 8·79. $C_{36}H_{54}O_8$ required: C, 70·33; H, 8·85%).

$LiAlH_4$ *Reduction of* VIb (I). VIb (0·1 g) in dry ether (30 ml) was stirred with $LiAlH_4$ (0·1 g) for 1·3 hr at 2°. After working up, the products were chromatographed on silica gel and recrystallization from MeOH gave VIII, as the main product, m.p. 280–282°, ν_{max}^{KBr} 3460, 3340, 1725 (sh), 1717 cm^{-1}. Acetylation of VIII with Ac_2O-pyridine gave IX (a single spot on TLC), δ 0·68, 0·75, 0·77, 0·82 (1Me each), 0·83 (d), 0·89 (d) (1Me each, J = 6 Hz), 2·00 (2 OAc), 2·11 (OAc), 3·68 (CH_2OAc, $COOCH_3$), 5·03 (1H, d, J_{AB} = 10 Hz), 5·27 (1H, sextet, J_{AB} = 10, J_{AX} = 10, J_{AY} = 5 Hz), 5·57 (1H, br). (2) VIb (0·2 g) in dry ether (60 ml) was refluxed with $LiAlH_4$ (1·2 g) for 5 hr. The products, containing VIb, VIII and X (main) were crystallized from MeOH–acetone, to give X, m.p. 258–260°, colourless crystals. Acetylation of X gave XI, m.p. 166–167·5° (from EtOH–H_2O), colourless crystals, and δ 0·69, 0·76, 0·81, 0·98 (1Me each), 0·82 (d), 0·88 (d) (1Me each, J = 6 Hz), 2·00, 2·03, 2·07, 2·11 (1 OAc each), 3·70 (CH_2OAc), 4·14, 4·33 (a pair of doublets, 1H each, J = 12 Hz), 4·9 –5·3 (2H), 5·44 (1H, br).

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