Phytochemistry, 1968, Vol. 7, pp. 773 to 782. Pergamon Press. Printed in England

HYDROXYBENZOQUINONES FROM MYRSINACEAE PLANTS—II.[1]

DISTRIBUTION AMONG MYRSINACEAE PLANTS IN JAPAN

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(*Received* 6 *September* 1967, *in revised form* 8 *November* 1967)

Abstract—The distribution of hydroxybenzoquinone derivatives in roots, rhizomes, barks and/or fruits of eleven species of Myrsinaceae was examined and the presence of embelin (Ia), rapanone (Ib), maesaquinone (IVa), acetylmaesaquinone (VI), 2-hydroxy-5-methoxy-3-pentadecenyl(tridecenyl- and tridecyl-)benzoquinone (VII) and ardisiaquinones A, B and C (VIII–X) in the plants was established (Table 2). The methods employed for the identification, especially for the alkyl homologues such as Ia and Ib, are described.

INTRODUCTION

MYRSINACEAE belongs to Primulales and about 1000 plants classified into thirty-three genera have been described.[2] Of these plants, eleven species grouped into three genera, *Ardisia*, *Myrsine* and *Maesa*, grow chiefly in southern parts of Japan.[3] From Myrsinaceae species 3,6-dihydroxy-2-alkylbenzoquinones, such as embelin (Ia), rapanone (Ib) and maesaquinone (IVa), and the methylene dimer, vilangin (V), have been isolated[4–15] and their structures have been elucidated[6, 12, 16, 17] (Table 1).

Although rapanone (Ib) has been isolated from the bulbs of *Oxalis purpurea* Linn. var. *jacquinii* Sonder (Geraniaceae)[18] and from the roots of *Connarus monocarpus* Linn. (Connaraceae)[19] and polygonaquinone (IVb), an alkyl homologue of maesaquinone (IVa) has been isolated from *Polygonatum falcatum* A. Gray (Liliaceae),[20] the distribution of these

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[1] Part I: H. OGAWA and S. NATORI, *Chem. Pharm. Bull. Tokyo* **13**, 511 (1965).

[2] *A. Engler's Syllabus der Pflanzenfamilien*, Vol. II, p. 390. Gebrüder Borntraeger, Berlin (1964).

[3] In this paper Ohwi's system of classification is adopted (J. OHWI, *Flora of Japan*, Shibundo, Tokyo (1964)). In Table 2 species names used by the authors of the previous chemical papers are also shown in parentheses.

[4] M. HIRAMOTO, *Yakugaku Zasshi* **59**, 665 (1939).

[5] J. KAWAMURA, *Repts Japan. Sci. Assoc.* **12**, 377 (1937).

[6] M. HIRAMOTO, *Yakugaku Zasshi* **62**, 460, 464 (1942).

[7] O. D. HENSENS and K. G. LEWIS, *Tetrahedron Letters* 4639 (1965).

[8] V. K. MURTHY, J. V. P. RAO and V. VENKATESWARLU, *Tetrahedron* **21**, 1445 (1965).

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[11] C. J. H. WARDEN, *Pharm. J.* (3), **18**, 601 (1888); **19**, 305 (1889).

[12] CH. B. RAO and V. VENKATESWARLU, *J. Org. Chem.* **26**, 4529 (1961).

[13] S. KRISHNA and B. S. VARMA, *Chem. Abs.* **37**, 3878 (1943).

[14] S. KRISHNA and B. S. VARMA, *J. Indian Chem. Soc.* **13**, 115 (1936).

[15] S. WILKINSON, *Planta Med.* **9**, 121 (1961).

[16] M. ASANO and K. YAMAGUCHI, *Yakugaku Zasshi* **60**, 105, 585 (1940).

[17] L. FIESER and E. M. CHAMBERLIN, *J. Am. Chem. Soc.* **70**, 71 (1948).

[18] O. FERNANDEZ and A. PIZARROSO, *Chem. Abs.* **42**, 8888 (1948).

[19] S. N. AIYAN, *Phytochem.* **3**, 335 (1964).

[20] H. NAKATA, K. SASAKI, I. MORIMOTO and Y. HIRATA, *Tetrahedron* **20**, 2319 (1964); K. YOSHIHIRA and S. NATORI, *Chem. Pharm. Bull. Tokyo* **14**, 1052 (1966).

hydroxybenzoquinone derivatives is assumed to be a chemotaxonomical characteristic of the Myrsinaceae.

TABLE 1. HYDROXYBENZOQUINONES FROM MYRSINACEAE SPECIES REPORTED IN THE LITERATURE

Name of plant*	Part used	Compound identified	References
Japanese origin			
Bladhia japonica Thunb.	rhizome	rapanone (?)	4
B. quinquegona (Blume) Nakai	bark	rapanone	5
B. sieboldii (Miq.) Nakai	bark	rapanone	5
Rapanea Maximowiczii Koidz.[24]	bark	rapanone	5
	wood	rapanone	5
R. neriifolia Mez	bark	rapanone	5
Maesa japonica (Thunb.) Moritzi	fruit	maesaquinone	1, 4, 6
Foreign origin			
Aegiceras corniculatum Blanco	bark	rapanone	7
Ardisia macrocarpa Wall.	bark	rapanone	8
	heartwood	rapanone	8
Embelia barbeyana Mez	root	embelin	9
E. kilimandscharica Gilg.	fruit	embelin	10
E. ribes Burm.	fruit	embelin	11
		vilangin	12
E. robusta Roxb.	fruit	embelin	13
Myrsine africana L.	fruit	embelin	10,14
M. capitellata Wall.	fruit	embelin	13
M. semiserrata Wall.	fruit	embelin	13
Rapanea neurophylla Mez	fruit	embelin	10
R. pulchra Gilg. et Schellens	root bark	rapanone	15
	bark	rapanone	15
	fruit	embelin	15

* Species names are those used by the authors of the original papers.

Recent discovery of ubiquinones (II) and plastoquinones (III) and of their role in electron transport system[21] urged us to work on the biochemical survey[22] of naturally occurring hydroxybenzoquinones[1, 23] and related compounds. In our previous paper[1] we have reported the confirmation of the structure of maesaquinone (IVa) and its occurrence in the form of a monoacetate (VI) in the fruits of *Maesa japonica* Moritzii. This paper deals with the results of screening all of the eleven species of Myrsinaceae growing in Japan.[3, 24] The detailed structural elucidations of the new compounds (VII–X) isolated in the course of study will be reported in a separate paper.[25]

[21] R. A. MORTON, editor, *Biochemistry of Quinones*, Academic Press, New York (1965).

[22] H. OZAWA, K. MOMOSE, S. NATORI, H. OGAWA and K. YAMAGUCHI, *Biochem. Biophys. Acta* **86**, 397 (1964); H. OZAWA, S. NATORI and K. MOMOSE, *Chem. Pharm. Bull. Tokyo* **13**, 1029 (1965); **15**, 1095 (1967); H. OZAWA, K. MOMOSE, M. MACHIDA, S. NATORI and K. YOSHIHIRA, *Chem. Pharm. Bull. Tokyo*, to be published.

[23] S. NATORI, H. OGAWA and H. NISHIKAWA, *Chem. Pharm. Bull. Tokyo*, **11**, 1343 (1963); **12**, 236 (1964); S. NATORI, Y. INOUE and H. NISHIKAWA, *Chem. Pharm. Bull. Tokyo* **15**, 380 (1967).

[24] We have not studied *Myrsine maximowiczii* (Koidz.) Walker (*Rapanea maximowiczii* Koidz., Japanese name: Shimataimintachibana) growing in Ogasawara Is., for the island has remained under the control of the U.S.A. since the Second World War.

[25] Preliminary communication of the results has been published (H. OGAWA, S. SAKAKI, K. YOSHIHIRA and S. NATORI, *Tetrahedron Letters* 1968, in press). The detailed paper will be published in *Chem. Pharm. Bull. Tokyo*. To be printed in No. 11 (TL-J-407).

RESULTS AND DISCUSSION

The plants and the parts used for the study are shown in Table 2. Since leaves and wood are generally not so rich in these compounds, they have not been examined except in a few cases.

Benzene or ethyl acetate extracts of the plants were examined by thin-layer chromatography and the results are shown schematically in Fig. 1. When positive results were obtained the extract prepared from larger amounts of material, if available, was purified by column or preparative thin-layer chromatography. The crystalline substances thus obtained were, after purification, identified by m.p. and mixed m.p. determinations, u.v. and i.r. spectra and thin-layer chromatography, compared with those of the authentic samples. Mass spectra are quite helpful for the identification of small amounts of material, while NMR spectra reveal the nature of the substituents.[25] The spectral data are summarized in Tables 3 and 4.

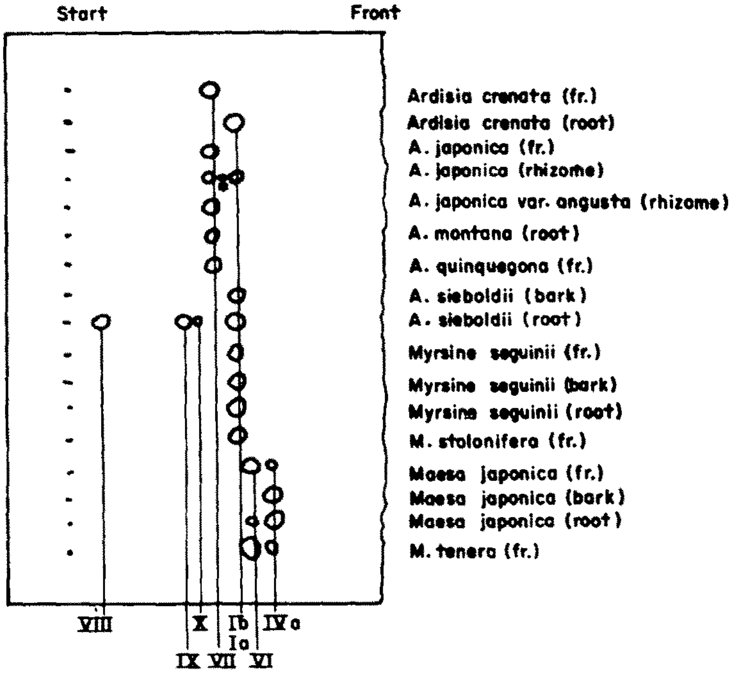

FIG. 1. THIN-LAYER CHROMATOGRAPHY OF HYDROXYBENZOQUINONE DERIVATIVES FROM MYRSINACEAE PLANTS.

(VIII) Ardisiaquinone A; (IX) ardisiaquinone B; (X) ardisiaquinone C; (VII) 2-hydroxy-5-methoxy-3-pentadecenylbenzoquinone; (Ia, Ib) embelin, rapanone; (VI) acetylmaesaquinone; (IVa) maesaquinone; *unidentified.

The results obtained are shown in Table 2. All of these plants, except *Ardisia crenata* forma *taquetii*, *A. crispa* and *A. pusilla*, showed the presence of benzoquinone derivatives. In the same plant, the constituents and their concentration vary from one part to another, fruits and bark generally containing larger amounts. Even in the same part of the same plant, materials collected at different places gave different results, as in the case of *Myrisine seguinii*.

Table 2. Distribution of hydroxybenzoquinone derivatives among Myrsinaceae species

Name of plant[3]	Japanese name	Part used	Date of collection	Place of collection	Amount of material (g)	Hydroxybenzo-quinone identified	Yield (%)	M.p. (°)
Ardisia crenata Sims.	manryo	root	Nov. 1964	Tosaurajiri, Tokushima	215	rapanone (embelin)[a]	0·008	141–142
		fruit	Nov. 1964	Tosaurajiri, Tokushima	107	the quinone (VII)[b]	0·006	69–73
A. crenata Sims. (f. *taquetii* (Lev.) Ohwi)	oomimanryo	fruit	Feb. 1966	Hachijo Is., Tokyo	64	(—)		
A. crispa (Thunb.) D.C.	karatachibana	root	Jan. 1964	Amagi, Shizuoka	70	(—)		
		fruit	Nov. 1964	Shizuoka, Shizuoka	20	(—)		
A. japonica (Thunb.) Blume. (*Bladhia japonica* Thunb.)	yabukoji	creeping rhizome[c]	Dec. 1963	Ebina, Kanagawa	1300	embelin (rapanone)[a] the quinone (VII) unidentified	0·001 0·01 0·0007	139–140 66·5–67 165
			Aug. 1964	Sayama, Saitama	1600			
			Nov. 1964	Sayama, Saitama	400			
			Jan. 1965	Sayama, Saitama	4300			
		fruit	Jan. 1965	Sayama, Saitama	400	the quinone (VII)[b]	0·06	61–67
A. japonica (Thunb.) Blume. var. *angusta* (Nakai) Makino et Nemoto	hosobaya-bukoji	creeping rhizome	May 1965	Osumi, Kagoshima	5	the quinone (VII)[b]	trace[d]	
A. montana (Miq.) Sieb.	ootsurukoji	creeping rhizome	Jan. 1966	Kiyosumi, Chiba	120	the quinone (VII)[b]	trace[d]	
A. pusilla D.C.	tsurukoji	creeping rhizome	Jan. 1965	Owase, Mie	100	(—)		
		fruit	Jan. 1965	Owase, Mie	10	(—)		
A. quinquegona Blume. (*B. quinquegona* (Blume.) Nakai)	shishiakuchi	root bark	Jan. 1965	Tanegashima, Kagoshima	75	(—)		
		bark[c]	Jan. 1965	Tanegashima, Kagoshima	100	(—)		
		fruit	Jan. 1965	Tanegashima, Kagoshima	149	the quinone (VII)[b]	0·003	79–81
A sieboldii Miq. (*B. sieboldii* (Miq.) Nakai)	mokutachibana	root bark[e]	Jan. 1965	Tanegashima, Kagoshima	1600	embelin, rapanone ardisiaquinone A B C	0·3 0·02 0·02 0·0005	144 154 119 69–70
			Jan. 1966	Tanegashima, Kagoshima	4850			
			Nov. 1966	Tanegashima, Kagoshima	8370			
		bark[c,f]	Jan. 1965	Tanegashima, Kagoshima	250	embelin, rapanone	0·02	138–141
		fruit	Jan. 1965	Tanegashima, Kagoshima	500	(—)		

Myrsine sequinii Lév. (*Rapanea neriifolia* Mez.)	taimintachi-bana	root	Mar. 1963	Yahatano, Shizuoka	580	(—)		
		root bark[g]	Jan. 1965	Tanegashima, Kagoshima	200	rapanone (embelin)[a]	0·5	141–144
		wood	Mar. 1963	Yahatano, Shizuoka	8240	(—)		
		bark[c]	Jan. 1965	Tanegashima, Kagoshima	200	rapanone (embelin)[a]	0·05	142–143
		fruit[h]	Jan. 1965	Tanegashima, Kagoshima	700	embelin	0·6	148–149
M. stolonifera (Koidz.) Walker	tsurumanryo	creeping rhizome	Oct. 1965	Yoshino, Mie	15	(—)		
		fruit	Jan. 1965	Yoshino, Mie	87	rapanone (embelin)[a]	0·02	142–143·5
Maesa japonica (Thunb.) Moritzii	izusenryo	root bark	Mar. 1965	Atami, Shizuoka	100	maesaquinone	0·03	123
						acetylmaesaquinone	0·005	—50
		bark	Mar. 1965	Atami, Shizuoka	100	maesaquinone	0·2	123
		fruit[c]	Nov. 1963	Atami, Shizuoka	(i)	maesaquinone	0·3	123
						acetylmaesaquinone[f]	5·0	28–34
M. tenera Mez.	shimaizusenryo	root bark	Jan. 1965	Tanegashima, Kagoshima	250	(—)		
		bark	Jan. 1965	Tanegashima, Kagoshima	250	(—)		
		fruit	Jan. 1965	Tanegashima, Kagoshima	64	maesaquinone	0·01	123
						acetylmaesaquinone	2·4	28–50

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[a] The compound in parentheses indicates the minor contaminant (cf. Fig. 2).

[b] They are assumed to be identical with the mixture from *A. japonica*.[25] Due to the scarcity of the sample further characterization has not been carried out.

[c] Cf. Table 1.

[d] Due to the small amount, they have not been isolated in crystalline state.

[e] The triterpene "ilexol", probably a mixture of bauerenol and baueradienol, and another triterpene mixture of m.p. 218° were isolated from the extract.

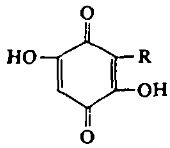
[f] "Ilexol" was also isolated.

[g] A mixture of protoanthocyanidines was obtained.

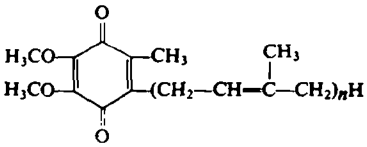
[h] In the course of separation a colourless compound assumed to be the corresponding hydroquinone, was separated but the purification was unsuccessful.

[i] See Ref. 1.

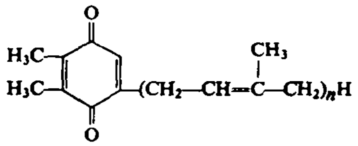
As far as we can see, embelin (Ia) and rapanone (Ib) normally co-exist in the same material, though the relative amounts of the two compounds differs from one material to another. The synthetic samples[16] of Ia and Ib and their mixture from plant materials did not show any noticeable difference in their behaviour on TLC, or in m.p. and u.v. spectra, and the separation is practically impossible. However, distinction is possible by careful examination of the region of 850–1000 cm^{-1} in the i.r. spectra (Fig. 2). In the mass spectra of Ia and Ib,



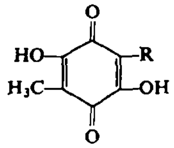
(Ia) R: $C_{11}H_{23}$
(Ib) R: $C_{13}H_{27}$



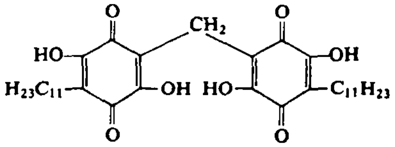
(II)



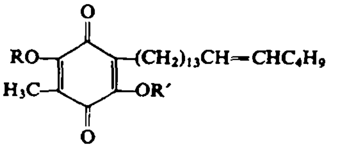
(III)



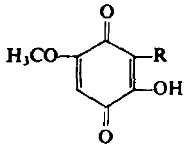
(IVa) R: —$(CH_2)_{13}CH{=}CHC_4H_9$
(IVb) R: —$C_{21}H_{43}$



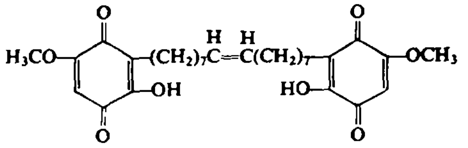
(V)



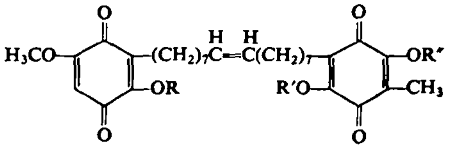
(VI)
R: H, R′: CH_3CO or
R: CH_3CO, R′: H



(VII) R: $C_{15}H_{29}$
($C_{13}H_{25}$)
($C_{13}H_{27}$)



(VIII)



(IX) R, R′, R″: H
(X) R: CH_3CO, R′, R″: H,
R′: CH_3CO, R, R″: H or
R″: CH_3CO, R, R′: H

M$^+$—CO peaks have not been observed under the conditions employed; thus the presence of the parent peaks (294 and 322 m/e) directly reflect the presence of Ia and Ib respectively (Table 4). The simplest method to check on their identity is by gas–liquid chromatography of the methyl esters of the fatty acids obtained by hydrogen peroxide oxidation, and the results obtained correlate well with observations of the i.r. spectra (Fig. 2). It thus becomes quite probable, that earlier reports of the isolation of Ia or Ib from natural resources might be untrue in that a mixture of both compounds was actually present,[26] and this phenomenon

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[26] Kawamura's authentic sample of rapanone[5] has been shown to be contaminated with embelin by these methods.

might be common with similar polyketides with long alkyl chains. Contrary to expectation, homologues of Ia and Ib, such as the compound having nonyl or pentadecyl side-chain, have not been identified. Maesaquinone (IVa), on the other hand, has already been proved not to be contaminated with similar homologues.[1]

From five *Ardisia* species a mixture of new benzoquinone derivatives has been isolated and shown to be 3-alkyl-2-hydroxy-5-methoxybenzoquinones (VII), the alkyl group being pentadecenyl, tridecyl and tridecenyl, the former being predominant in the case of the mixture from *Ardisia japonica.*[25] From the root bark of *A. sieboldii* three novel bisbenzoquinones, designated ardisiaquinones A, B and C, have been isolated and shown to be VIII–X.[25] Since vilangin (V)[12] and its homologues are expected to be rather insoluble in the solvents employed for extraction, the residues were further extracted by dioxane. However, there was no sign of the presence of these methylene dimers in the plants examined.

TABLE 3. ULTRA-VIOLET AND INFRARED SPECTRA OF HYDROXYBENZOQUINONE DERIVATIVES FROM MYRSINACEAE SPECIES[a]

Compound	Ultra-violet λ_{max}^{EtOH} nm (log ε)		ν_{OH} cm^{-1}	Infrared (KBr) $\nu_{C=O}$ ($\nu_{C=C}$) cm^{-1}
Embelin (Ia)	292·5 (4·24)	426 (2·53)	3305	1637 (sh), 1605 (s)
Rapanone (Ib)	292·5 (4·24)	425 (2·43)	3305	1605 (s)
Maesaquinone (IVa)	295 (4·36)	440 (2·58)	3320	1605 (s)
Acetylmaesaquinone (VI)	275 (4·18)	415 (2·85)	3315	1782 (s), 1655 (s), 1639 (sh), 1615 (m)
2-Hydroxy-5-methoxy-3-pentadecenyl-(tridecenyl-, tridecyl-)benzoquinone (VII)[b]	289 (4·21)	420 (2·74)	3318	1655 (sh), 1632 (m), 1595 (s)
Ardisiaquinone A (VIII)	289 (4·60)	422 (2·83)	3320	1655 (sh), 1633 (m), 1598 (s)
Ardisiaquinone B (IX)	291 (4·56)	424 (2·82)	3300	1605 (s)
Ardisiaquinone C (X)	281 (4·40)	420 (2·87)	3328	1774 (s), 1657 (sh), 1635 (m), 1603 (s)

[a] The correlation between the structures and u.v. and i.r. spectra has been reported.[1,20,23,25]

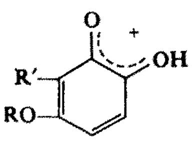
[b] Log ε is calculated as 3-pentadecenyl.

From the results embelin (Ia) and rapanone (Ib) have been shown to be widely distributed in both *Ardisia* and *Myrsine* species, while maesaquinone (IVa) and its acetate (VI) are restricted to *Maesa.* The new methoxy derivatives (VII) and the novel bisbenzoquinones (VIII–X) have only been isolated from *Ardisia* species. Since the corresponding hydroquinone derivatives of these compounds are sensitive for aerial oxidation, it seems possible that they might exist in the bound forms such as a glycoside in the living plant, though this appears to be unlikely in the case of the fruits of *Maesa japonica.*[1] It is also probable that methoxyl derivatives like VII–X and acetyl derivatives like VI are more widely distributed in living plants than hitherto recognized, since they are easily hydrolysable, especially in alkaline conditions.[1,25]

TABLE 4. MASS SPECTRA OF HYDROXYBENZOQUINONE DERIVATIVES FROM MYRSINACEAE SPECIES[a, b] m/e (RELATIVE INTENSITY)

	Fragment									
Compound	a	b	c	d	e	f[b]	g	M^+-28 and M^++2-28	M^+	M^++2[b]
Embelin (Ia)	125 (10)		142 (22)	153 (26)	154 (100)	155 (38)			294 (30)	
Rapanone (Ib)	125 (11)		142 (23)	153 (28)	154 (100)	155 (40)			322 (31)	
Maesaquinone (IVa)	139 (11)			167 (25)	168 (52)	169 (51)			418 (100)	420 (6)
2-Hydroxy-5-methoxy-3-pentadecenylbenzoquinone (VII)	139 (14)	153 (16)	156 (11)	167 (18)	168 (100)	169 (64)			334 (12), 336 (13), 362 (50)	364 (13)
Ardisiaquinone A (VIII)	139 (50)	153 (31)		167 (31)	168 (80)	169 (100)	193 (19)	500 (9)	528 (50)	530 (31)
Ardisiaquinone B (IX)	139 (39)	153 (26)		167 (24)	168 (82)	169 (100)	193 (16)	500 (7), 502 (7)	528 (97)	530 (48)

a



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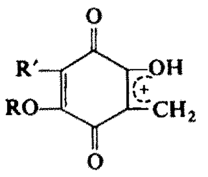

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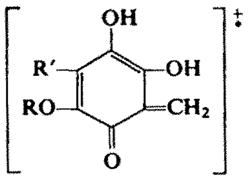

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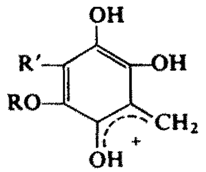

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[a] Determined on a Hitachi RMU-6D Mass Spectrometer with direct inlet system. Ionization potential: 70 eV; ionization temperature: *ca.* 200°.

[b] For the fragmentations of benzoquinone derivatives, see: R. T. APLIN and W. T. PIKE, *Chem. & Ind.* 20009 (1966); H. MORIMOTO, T. SHIMA, I. IMADA, M. SASAKI and A. OUCHIDA, *Ann.* **14**, 1052 (1966), and the references cited therein. Further details will be discussed in the forthcoming paper.[25]

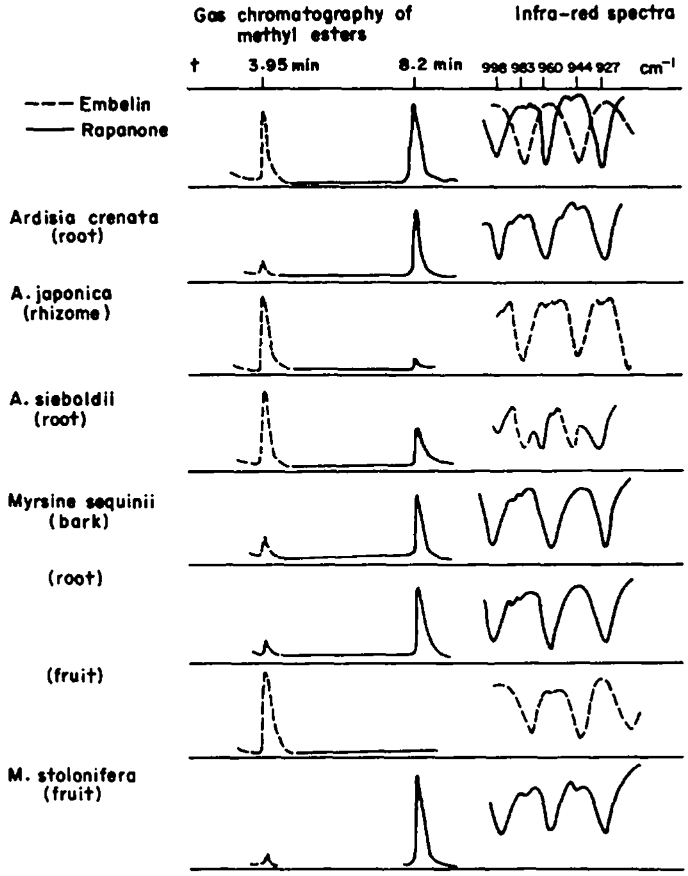

FIG. 2. THE i.r. SPECTRA OF MIXTURES OF EMBELIN AND RAPANONE AND THE GAS CHROMATOGRAPHY OF THE METHYL ESTERS OF THE OXIDATION PRODUCTS.

EXPERIMENTAL

Extraction

The dried material was extracted with boiling benzene or ethyl acetate for several hours and the residue, after the evaporation of the solvent, was used for TLC. For the isolation of constituents, extraction was repeated several times until the extract became almost colourless.

Thin-layer Chromatography

Silica gel G (nach Stahl, E. Merck) impregnated with 3 per cent oxalic acid solution and dried was employed with a mixture of benzene–ethyl acetate (10:2) or benzene. Ammonia was used for detection of the hydroxybenzoquinone derivatives.

Isolation of the Quinones

The extract was dissolved in hexane or benzene and the solution introduced onto a column of $CaHPO_4$ or acid-washed silica gel (Mallinckrodt, 100 mesh) and eluted successively with hexane, hexane–benzene, benzene and benzene–ethyl acetate. Each fraction was examined by TLC and the column chromatography repeated, if necessary. For the separation of acetylmaesaquinone (VI), preparative thin-layer chromatography was employed.[1] Fractions containing the required compound were combined and evaporated. In some cases, washing with cold hexane was ample for the purification of the extract and chromatography was not used for the isolation. The residue showing a single spot on TLC was recrystallized from benzene or ethanol (Ia, Ib and IVa), from 80 per cent methanol (VII) or from benzene–hexane (VIII–X) until it showed a sharp melting point.

Alkaline Hydrogen Peroxide Oxidation of Quinones and Gas Chromatography of the Fatty Acids

A mixture of embelin (Ia) and rapanone (Ib) (2–3 mg) was dissolved in *N*-KOH and H_2O_2 (30 per cent, 0·1–0·2 ml) was added under slight warming on a water bath. After 3 hr the reaction mixture was acidified and extracted with ether. The ethereal layer was dried, evaporated and methylated with CH_2N_2 in ether. The mixture of the methyl esters was applied onto a Hitachi-Perkin Elmer Gas Chromatograph F6D equipped with a column of 0·3 × 200 cm packed with SE 52 (5 per cent) on Chromosorb W at 200°. The retention times were compared with the methyl esters prepared from authentic fatty acids and identified.

Acknowledgements—The authors' thanks are due to Mr. M. Taki, Mr. Y. Miyazaki and Mr. M. Satake, this Institute, and to Mr. I. Sasaki, Tsumura Laboratory, for their kind co-operation in the collection and identification of plant materials. We are grateful to Professor T. Kariyone, Drs. K. Yamaguchi and T. Shimomura for their interests in this work. The authors are indebted to Dr. T. Miki, Takeda Chemical Industries Ltd., and Dr. T. Oba and Miss R. Koyama, this Institute, for spectral determinations.