

A Group of Unusual Seed Oils

KLAUS SERCK-HANSEN

Institute of Medical Biochemistry, University
of Gothenburg, Göteborg, Sweden

A thick, levo-rotatory oil ($[\alpha]_D^{25} - 14^\circ$ (neat), -26° (6% in pyridine)) with high refractive index ($n_D^{25} 1.493$) and high density ($d_4^{25} 0.956$) can be extracted from seeds of *Coriaria myrtifolia* L. (family Coriariaceae¹). Thin-layer chromatography of this and seven other *Coriaria* oils shows (Fig. 1) that they are all very similar. Data reported below indicate that seeds of *C. myrtifolia* contain a triglyceride oil with fatty acids of the following approximate composition: 1–2% minor components, 3% palmitic acid (16:0), 1–2% stearic acid (18:0), 9% 18:1 (mainly oleic acid), 14% 18:2 (mainly linoleic acid), 1% 18:3, and 70% 13*R*-hydroxy-9-*cis*,11-*trans*-octadecadienoic acid, 18:2(9*c*,11*t*,13*R*-OH).

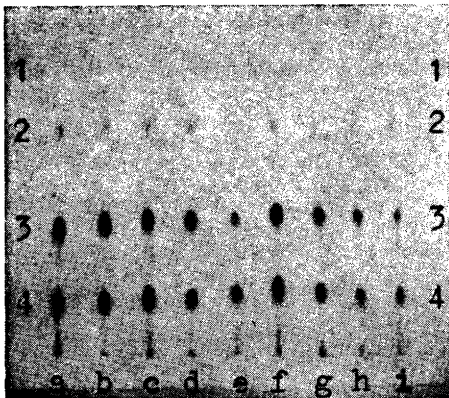


Fig. 1. Thin-layer chromatogram of *Coriaria* oils run with 1% methanol in chloroform on silica gel (G) and made visible in iodine vapour. a) *C. myrtifolia*, b) *C. japonica*, c) *C. nepalensis*, d) *C. papuana*, e) *C. ruscifolia*, f) *C. sarmentosa*, g) *C. terminalis*, h) *C. terminalis* var. *xanthocarpa*, i) *C. myrtifolia*. The fractions 1 to 4 apparently correspond to triglycerides with from 0 to 3 hydroxy acids, respectively. Fraction 4 is therefore probably a single triglyceride species. It moves behind the corresponding fraction in castor oil, but ahead of that in *Dimorphotheca sinuata* seed oil, rich in 18:2(10*t*,12*t*,9-OH).²

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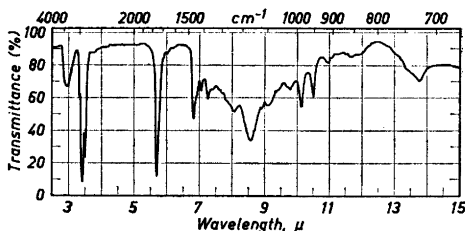


Fig. 2. Infrared spectrum of *Coriaria myrtifolia* seed oil (neat).

A recent communication³ appearing after the work reported here had been done, shows that principal fatty acid from seed oil of *Coriaria nepalensis* Wall. also has the structure 18:2(9*c*,11*t*,13*R*-OH); the name coriolic acid is proposed for it. No other natural products have been reported to be rich sources of this unusual fatty acid.

The infrared spectrum of *C. myrtifolia* seed oil (Fig. 2) is of the triglyceride type,⁴ but with strong bands due to unesterified hydroxyl groups (2.95 μ) and *cis-trans*-diene conjugation (10.15 μ and 10.5 μ).⁴ The ultraviolet spectrum also shows strong diene absorption ($\lambda_{\max}^{\text{hexane}}$ 235 $m\mu$, $E_1^{1\% \text{ cm}}$ 635).⁴ Acid-catalysed methanolysis of the oil yielded a product without infrared hydroxyl absorption but with a strong band indicating triene conjugation (10.05 μ), confirmed by ultraviolet analysis ($\lambda_{\max}^{\text{hexane}}$ 259–269–280 $m\mu$).⁴ Gas chromatography of the methanolysed oil gave the following main peaks: 3% 16:0, 1–2% 18:0, 9% 18:1, 14% 18:2, 1% 18:3, and 70% complex 18:3 (conjugated). After catalytic hydrogenation the peaks corresponded to 4% palmitate and 96% stearate. The presence of a conjugated allylic dienol system in the native oil was thus indicated,⁵ and could be confirmed by oxidation of the oil with chromium trioxide in pyridine: the product obtained exhibited strong conjugated dienone absorption² both in the ultraviolet ($\lambda_{\max}^{\text{hexane}}$ 270 $m\mu$) and in the infrared spectrum (Fig. 3). The double carbonyl band (between 5.9 and 6.0 μ) suggests that the double bond next to the carbonyl group is *trans*.^{6–8} Isomerisation to an all-*trans* structure had not occurred during the oxidation, as evidenced by a diene doublet⁴ (10.0 μ and 10.4 μ) in

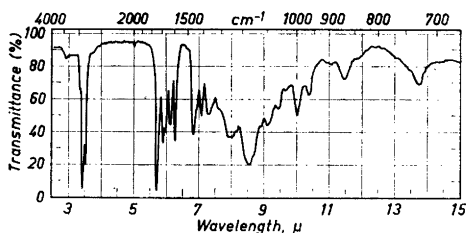


Fig. 3. Infrared spectrum (neat liquid) of *Coriaria myrtifolia* seed oil oxidized with chromium trioxide in pyridine.

the region where a similar all-*trans* dienone has a single band.²

The dienol system was located by permanganate oxidation of the acetylated oil and isolation of two major cleavage products: one shown by infrared analysis before and after hydrolysis to contain much α -acetoxy acid, and the other an acid glyceride fraction shown by gas chromatography to yield dimethyl nonanedioate as main ester on acid-catalysed methanolysis. In agreement with the presence of a 13-hydroxyl group, permanganate oxidation of the native oil produced hexanoic acid as main mono-carboxylic acid, whereas castor oil gave heptanoic acid; small amounts of nonanoic acid were also formed in both cases.

On catalytic hydrogenation the acetylated oil took up about twice as much hydrogen as the same amount of acetylated castor oil. Both saturated products were weakly dextro-rotatory. If these activities are mainly due to the asymmetric acetoxy-bearing carbon atoms, the absolute configurations at these points should be the same. This was confirmed by preparation of the chloralides⁹ from the α -acetoxy acids formed by oxidative degradation of the acetylated oils: both products were dextro-rotatory. As ricinoleic acid is known to have the 12D-OH configuration,¹⁰ the principal *C. myrtifolia* acid must have the 13D-OH or *R* configuration.

Gas chromatography of the product obtained by methanolysis of the acetylated and hydrogenated oil gave peaks corresponding to about 4% palmitate, 26% stearate, and 70% hydroxystearate. The melting-point (53–54°C), infrared spectrum, and mass spectrum of the collected hydroxystearate fraction were practically the same as for racemic methyl 13-hydroxystearate.¹¹

As similar oils,^{12,13} *Coriaria* oils may be of interest to industry. Seeds from sun-dried fruits of *C. myrtifolia* contain about 30% oil and the kernels nearly 70%. Oil extracted and stored in the laboratory appears to be quite stable, and oil from twelve years old seeds from a herbarium specimen of *C. japonica* gave the same infrared spectrum as oil from new seeds of *C. myrtifolia*. Wild plants of *C. myrtifolia* may be laden with fruits which often dry on the branches. The leaves have been used for tanning, and other members of the genus are also rich in tannins.¹⁴ Their toxic sesquiterpene coriamyrtin¹⁴ appears to have been commercially available for medical use.¹⁵ Some of the species are reported to fix atmospheric nitrogen, and this capacity suggests that they may improve soil fertility and thrive in agriculturally uneconomic regions.¹⁶

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1. Good, R. D'O. *New Phytologist* **29** (1930) 170.
2. Binder, R. G., Applewhite, T. H., Diamond, M. J. and Goldblatt, L. A. *J. Am. Oil Chemists' Soc.* **41** (1964) 108.
3. Tallent, W. H., Harris, J., Wolff, I. A. and Lundin, R. E. *Tetrahedron Letters* **1966** 4329.
4. Chapman, D. *The Structure of Lipids by Spectroscopic and X-Ray Techniques*, Methuen, London 1965.
5. Smith, C. R., Jr., Wilson, T. L., Melvin, E. H. and Wolff, I. A. *J. Am. Chem. Soc.* **82** (1960) 1417.
6. Bell, I., Jones, E.R.H. and Whiting, M. C. *J. Chem. Soc.* **1958** 1313.
7. Noack, K. and Jones, R. N. *Can. J. Chem.* **39** (1961) 2225.
8. Kronenberg, M. E. and Havinga, E. *Rec. Trav. Chim.* **84** (1965) 17, 979.
9. Wallach, O. *Ann.* **193** (1878) 1.
10. Serck-Hanssen, K. *Chem. Ind. (London)* **1958** 1554.
11. Bergström, S., Aulin-Erdtman, G., Roland, B., Stenhagen, E. and Östling, S. *Acta Chem. Scand.* **6** (1952) 1157.

12. Earle, F. R., Mikolajczak, K. L., Wolff, I. A. and Barclay, A. S. *J. Am. Oil Chemists' Soc.* **41** (1964) 345.
13. Barclay, A. S. and Earle, F. R. *Econ. Botany* **19** (1965) 33.
14. Hegnauer, R. *Chemotaxonomie der Pflanzen*, Birkhäuser, Basel und Stuttgart 1964, Vol. 3, p. 562.
15. *Chem. Centr.* **70 I** (1899) 706; *Jahresbericht, E. Merck* **1898** 25.
16. Allen, E. K. and O. N. *Proc. 25th Biol. Colloq. (1964) on Microbiology and Soil Fertility*, Oregon State University Press, Corvallis 1965, p. 77.

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On the Action of *t*-Butyl Hypochlorite on *m*-Cresol

ARNE BRÄNDSTRÖM and
STIG A. I. CARLSSON

*Chemical Research Laboratory, AB Hässle,
Göteborg, Sweden*

In a paper by Ginsburg,¹ the action of *t*-butyl hypochlorite on *m*-cresol is reported. In this reaction, a compound with m.p. 55–56.5°C was obtained and it was stated to be 2-chloro-3-methylphenol since the melting point agreed with that reported by Gibson² in his preparation of the same compound in an unambiguous way.

In our search for a convenient method to prepare 2-chloro-3-methylphenol, we attempted the chlorination of *m*-cresol with *t*-butyl hypochlorite, and after fractionation of the reaction mixture, we also obtained a product with m.p. 57°C. However, as the NMR spectrum indicated, this product was not homogeneous but a mixture of 4- and 6-chloro-3-methylphenol which were separable by recrystallization from petroleum ether.

Gas chromatographic and infrared analysis of the crude chlorination mixture proved the main product to be 4-chloro-3-methylphenol. The mixture contained only about 15% 2-chloro-3-methylphenol. Thus, Ginsburg's statement¹ that the main product obtained by the action of *t*-butyl hypochlorite on *m*-cresol is 2-chloro-3-methylphenol, is not correct.

However, the result is in good agreement with that obtained in the chlorination of *m*-cresol with chlorine.³

Experimental. Melting points were determined on a Kofler hot-stage microscope and are corrected. A Perkin-Elmer model 337 spectrophotometer was used for the IR-absorption measurements. The gas chromatographic analyses were performed on a Perkin-Elmer 800 instrument using a $78 \times \frac{1}{4}$ in column packed with Apiezon L (5%) on HMDS-treated Chromosorb W (80–100 mesh).

Chlorination of m-cresol. This was performed according to the procedure of Ginsburg.¹ After evaporation of carbon tetrachloride and *t*-butanol the crude residue was analysed by gas chromatography giving the following composition: 49% 4-chloro-3-methylphenol, 44% 2- and 6-chloro-3-methylphenol and 7% unreacted *m*-cresol. As the 2- and 6-chloro-*m*-cresols could not be separated by gas chromatography they were determined by infrared analysis using the peaks at 605 and 709 cm⁻¹. The ratio of 2- to 6-chloro-*m*-cresol was about 1:2.

Samples of chloro-*m*-cresols for identification of the peaks in the gas chromatograms and the infrared spectra were obtained as follows:

2-Chloro-3-methylphenol. This compound was prepared by standard methods by the sequence: 2-methylaniline → 2-methyl-6-nitroaniline → 2-chloro-3-nitrotoluene → 2-chloro-3-methylaniline → 2-chloro-3-methylphenol. After recrystallization from petroleum ether the m.p. was 50–51°; lit.² 55–56°.

6-Chloro-3-methylphenol. Prepared from 6-chloro-3-methylaniline by diazotization and replacement of the diazonium group by hydroxyl. Recrystallization from petroleum ether, m.p. 46–46.5°; lit.³ 45–46°.

4-Chloro-3-methylphenol. A commercial product was recrystallized from petroleum ether, m.p. 66°; lit.⁴ 66°.

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1. Ginsburg, D. *J. Am. Chem. Soc.* **73** (1951) 2723.
2. Gibson, G. P. *J. Chem. Soc.* **1926** 1425.
3. Hodgson, H. H. and Moore, F. H. *J. Chem. Soc.* **1926** 2038.
4. Sah, P. P. T. and Anderson, H. H. *J. Am. Chem. Soc.* **63** (1941) 3164.

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